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[ PHYSICAL SCIENCES INCLUDING MATHEMATICS ]

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Part II

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# EQUILATERAL AND EQUIANGULAR POLYGONS IN SPACE

By

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1 Apart from its general mathematical interest, the problem of the existence and construction of equilateral and equiangular polygons in space is of particular interest to the Organic Chemist as it throws light on the structure of closed ring compounds of carbon. Sachse<sup>1</sup> seems to have tackled it first in 1890 and has obtained valuable results, as also Mohr,<sup>2</sup> Derx,<sup>3</sup> Wightman<sup>4</sup> and other chemists, but no systematic mathematical treatment appears to have been given until 1929, when Brodetsky<sup>5</sup> discussed the question in some detail. The method used by him, however, is somewhat indirect and the discussion of the hexagon is incomplete. The following treatment is both simpler and more direct and does not require any mathematical equipment beyond elementary trigonometry and geometry. The different possibilities for the hexagon are discussed more thoroughly and results not noticed by Brodetsky are obtained. A purely geometrical explanation for the existence of the flexible hexagon is also given and is, of course, more satisfactory than the analytical discussion.

A simple method for constructing models to illustrate the results is also described.

2 The problem is to construct equilateral and equiangular polygons, which are not necessarily plane. In all cases we shall take each side of the polygon to be of length  $a$ , and each angle of the polygon to be  $\pi - \theta$ , so that each *exterior* angle is  $\theta$  (given). Then A, B, C, D, . . . being consecutive vertices, the lines AC, BD, CE, . . . joining alternate vertices are each of length  $2a \cos \frac{\theta}{2}$ . Again the perpendicular from any vertex (e.g. B) on the line joining the two adjacent vertices (i.e. AC) is of constant length, viz.  $a \sin \frac{\theta}{2}$  (fig. 1). Let  $a \cos \frac{\theta}{2} = b$  and  $a \sin \frac{\theta}{2} = c$ . The diagonal joining any

Fix ACE first and let L, M, N be the midpoints of the sides CE, EA and AC respectively. Then  $DL = FM = BN = c = a \sin \frac{\theta}{2}$  and they are perpendicular to CE, EA and AC respectively, (fig 5). Let  $\alpha, \beta, \gamma$  be the angles made by LD, MF and NB with the plane ACE, i.e. with the lines AL, CM and EN respectively, the angles being reckoned positive on one side of the plane and negative on the other. We may then express the conditions that

$$BD = DF = FB = 2b$$

Let  $B', F'$  be the projections of B, F on the plane ACE. Then  $B'F'^2 = OB'^2 + OF'^2 - 2 OB' \cdot OF' \cos 120^\circ$ .

$$\begin{aligned} &= (b/\sqrt{3} + c \cos \gamma)^2 + (b/\sqrt{3} + c \cos \beta)^2 \\ &\quad - 2 (b/\sqrt{3} + c \cos \beta) (b/\sqrt{3} + c \cos \gamma) (-\frac{1}{2}) \\ &= b^2 + c^2 (\cos^2 \beta + \cos^2 \gamma) + \sqrt{3} bc (\cos \beta + \cos \gamma) \\ &\quad + c^2 \cos \beta \cos \gamma \end{aligned}$$

The projection of BF perpendicular to ACE =  $c (\sin \beta \sim \sin \gamma)$ .

$$\begin{aligned} \therefore BF^2 &= B'F'^2 + (\perp \text{ projection})^2 \\ &= b^2 + 2c^2 + \sqrt{3} bc (\cos \beta + \cos \gamma) \\ &\quad + c^2 (\cos \beta \cos \gamma - 2 \sin \beta \sin \gamma). \end{aligned}$$

But  $BF = 2b$

Therefore,

$$\sqrt{3} bc (\cos \beta + \cos \gamma) + c^2 (\cos \beta \cos \gamma - 2 \sin \beta \sin \gamma) = 3b^2 - 2c^2.$$

In the same way equating BD and DF to  $2b$ , we have

$$\sqrt{3} bc (\cos \gamma + \cos \alpha) + c^2 (\cos \gamma \cos \alpha - 2 \sin \gamma \sin \alpha) = 3b^2 - 2c^2$$

and 
$$\sqrt{3} bc (\cos \alpha + \cos \beta) + c^2 (\cos \alpha \cos \beta - 2 \sin \alpha \sin \beta) = 3b^2 - 2c^2$$

We may write these as

$$p (\cos \beta + \cos \gamma) + q (\cos \beta \cos \gamma - 2 \sin \beta \sin \gamma) = 1 \quad (1)$$

$$p (\cos \gamma + \cos \alpha) + q (\cos \gamma \cos \alpha - 2 \sin \gamma \sin \alpha) = 1 \quad (2)$$

$$p (\cos \alpha + \cos \beta) + q (\cos \alpha \cos \beta - 2 \sin \alpha \sin \beta) = 1. \quad (3)$$

where  $p = \sqrt{3} bc / (3b^2 - 2c^2) = \sqrt{3} \sin \theta / (1 + 5 \cos \theta)$ . (a)

and  $q = c^2 / (3b^2 - 2c^2) = (1 - \cos \theta) / (1 + 5 \cos \theta)$ . (b)

Note that  $p^2 = 2q^2 + q$ . (c)

The values of  $\alpha, \beta, \gamma$  obtained from (1), (2), (3) will fix the hexagon required.

The equations are obviously satisfied if  $\alpha = \beta = \gamma$ , and

$$2p \cos \alpha + q (\cos^2 \alpha - 2 \sin^2 \alpha) = 1$$

$$\text{giving } \cos \alpha = \frac{-p \pm \sqrt{p^2 + 6q^2 + 3q}}{3q}$$

$$= -\sqrt{3} \cot \frac{\theta}{2} \text{ or } \frac{1}{\sqrt{3}} \cot \frac{\theta}{2} \text{ from (a), (b) and (c).}$$

6(1) If  $\theta < 60^\circ$ ,  $\cot \theta/2 > \sqrt{3}$  and so both solutions are inadmissible as they would give imaginary values for  $\alpha$ .

6(2) If  $\theta \geq 60^\circ$ , the second solution gives a real acute value for  $\alpha$ , but the first one is inadmissible unless  $\left| \cot \theta/2 \right| \leq \frac{1}{\sqrt{3}}$ , i.e. unless  $\theta \geq 120^\circ$ .

6(3)  $\theta \geq 120^\circ$ , both values of  $\cos \alpha$  are admissible

Thus if  $\theta$  lies between  $60^\circ$  and  $120^\circ$ , there is one hexagon for each value of  $\theta$ , with  $\alpha = \beta = \gamma$ , and if  $\theta \geq 120^\circ$  there are two such hexagons, [see figs. 6 (a) and 8, and further geometrical discussion in §9].

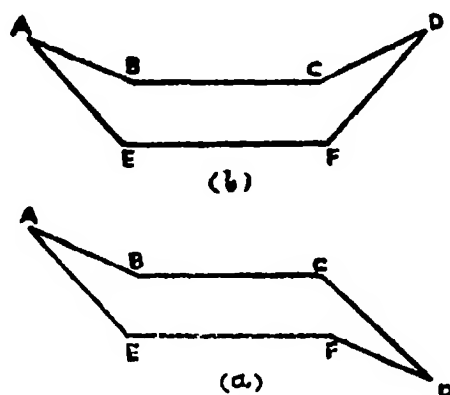


FIG 6 (a) & (b)

7. To investigate the existence of hexagons for which  $\alpha, \beta, \gamma$  are not all equal, we proceed as follows

From equations (1) and (2), taking (a), (b), (c), into account we obtain,

$$\frac{\cos \gamma}{\sin \alpha - \sin \beta - p \sin (\alpha - \beta)} = \frac{\sin \gamma}{(q+1)(\cos \alpha - \cos \beta)} = -\frac{1}{p(\sin \alpha - \sin \beta) + q \sin (\alpha - \beta)}$$

Putting  $\alpha + \beta = 2x$  and  $\alpha - \beta = 2y$ , these reduce to

$$\frac{\cos \gamma}{2 \sin y \cos x - 2p \sin y \cos y} = \frac{\sin \gamma}{-2(q+1) \sin x \sin y} = -\frac{1}{2p \sin y \cos x + 2q \sin y \cos y}$$

$$\therefore \sin y = 0; \text{ i.e. } \alpha = \beta \text{ or} \quad (4)$$

$$\frac{\cos \gamma}{\cos x - p \cos y} = \frac{\sin \gamma}{-(q+1) \sin x} = -\frac{1}{p \cos x + q \cos y} \quad (5)$$



Eliminating  $\Upsilon$  and using (a), (b), (c) we have

$$3q(q+1)\cos^2x - q(q+1)\cos^2y + 2p(q+1)\cos x \cos y = (q+1)^2$$

$$\therefore q+1=0; \text{ or } 2+4\cos\theta=0; \text{ or } \theta=120^\circ \quad (6)$$

or

$$3q\cos^2x - q\cos^2y + 2p\cos x \cos y = q+1 \quad (7)$$

Putting  $\alpha + \beta$  for  $2x$  and  $\alpha - \beta$  for  $2y$ , this becomes

$$\frac{3q}{2} \left\{ \cos(\alpha + \beta) + 1 \right\} - \frac{q}{2} \left\{ \cos(\alpha - \beta) + 1 \right\} \\ + p(\cos \alpha + \cos \beta) = q+1$$

or  $p(\cos \alpha + \cos \beta) + q(\cos \alpha \cos \beta - 2 \sin \alpha \sin \beta) = 1$   
which is identical with equation (3)

This is a surprising and unexpected result and means that equations (1), (2) and (3) are not all independent, but reduce to only two independent equations. We may, therefore, assign any value (within certain limits) to one of the angles,  $\Upsilon$  say, and we can find suitable values of  $\alpha$  and  $\beta$  to satisfy the required conditions. The polygon so obtained is thus continuously deformable, having one degree of freedom, corresponding to the co-ordinate  $\Upsilon$ .

To consider the limits within which  $\Upsilon$  may vary, let us start with the symmetrical position in which  $\alpha = \beta$ .

Equations (1) and (2) of §6 show that we may regard  $\alpha, \beta$  as the roots of the following equation in  $\phi$

$$p(\cos \phi + \cos \Upsilon) + q(\cos \phi \cos \Upsilon - 2 \sin \phi \sin \Upsilon) = 1$$

If then the roots of this equation are equal, we find

$$(p \cos \Upsilon - 1)^2 = (p + q \cos \Upsilon)^2 + 4 q^2 \sin^2 \Upsilon$$

giving

$$\cos \Upsilon = \frac{p}{q} = \sqrt{3} \cot \frac{\theta}{2}$$

$$\text{or } \cos \Upsilon = \frac{p(1-3q)}{q(5q+1)} = \frac{(4 \cos \theta - 1)}{\sqrt{3}} \cot \frac{\theta}{2}$$

Neither of these values coincides with those obtained for  $\cos \Upsilon$  (or  $\cos \alpha$ ) in §6, which shows that the form obtained there, with  $\alpha = \beta = \Upsilon$  is a distinct form and not a particular case of the deformable polygon, now obtained. The form in §6 is therefore rigid and non-deformable. Now considering that values for  $\Upsilon$  must be real, we have

$$\cos \Upsilon = \frac{(4 \cos \theta - 1)}{\sqrt{3}} \cot \frac{\theta}{2} \text{ if } 60^\circ \leq \theta \leq 120^\circ$$

and  $\cos \Upsilon = \sqrt{3} \cot \frac{\theta}{2} \text{ if } \theta \geq 120^\circ$

In either case, it can be further seen that when  $\alpha$  and  $\beta$  are positive  $\gamma$  is negative [fig 6 (b).]

From the symmetry of the figure, we can now deduce that any increase of  $\alpha$  leads to a decrease of  $\beta$  and vice versa, the corresponding value of  $\gamma$  has therefore a turning value in this position. This gives therefore the limits, within which  $\gamma$  (or  $\alpha$  or  $\beta$ ) must lie, as  $\pm \cos^{-1} \left\{ \frac{4 \cos \theta - 1}{\sqrt{3}} \cot \frac{\theta}{2} \right\}$  if  $\theta$  lies between  $60^\circ$  and  $120^\circ$ , and  $\pm \cos^{-1} (\sqrt{3} \cot \frac{\theta}{2})$  if  $\theta > 120^\circ$

If we vary  $\gamma$ , starting from this extreme negative position, one of the angles,  $\alpha$  say, increases and the other decreases. When  $\alpha$  reaches its maximum positive value,  $\beta$  and  $\gamma$  become equal both being negative. If  $\gamma$  increases still further,  $\beta$  continues to decrease and reaches its maximum negative value when  $\gamma$  becomes equal to  $\alpha$ , both being positive, and so on.

8 We now consider equation (6) of §6 viz  $q + 1 = 0$  or  $\theta = 120^\circ$ . If we substitute this value in equation (5) of §6, we obtain  $\gamma = 180^\circ$ ,  $\alpha$  and  $\beta$  being perfectly arbitrary. The figure then consists of two equilateral triangles ABC, DEF with A and D coincident and AB inclined at an angle of  $60^\circ$  with DE, the positions of the triangles being otherwise arbitrary. There are thus two degrees of freedom corresponding to the co ordinates  $\alpha$  and  $\beta$ .

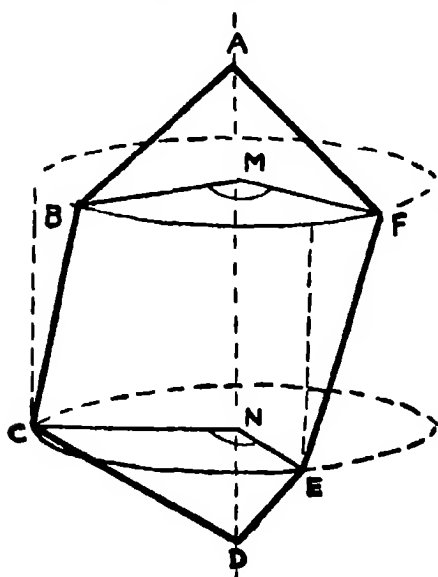


FIG. 7

9 We shall now obtain purely geometrical constructions for such hexagons, which give us an insight into their nature.

Let ABCD be a quadrilateral having  $AB = BC = CD = a$  and  $AC = BD = 2b$ . Whether it is plane or skew, it can be easily seen that AB and CD make equal angles with AD. Take next an exactly identical quadrilateral AFED and superpose it on the first. If we now rotate AFED about the axis AD so as to make the angle  $BAF = 180^\circ - \theta$ , we should obtain the required hexagon,

provided angle CDE is also equal to  $180^\circ - \theta$ . That this is so can be seen from figure 7, for since AD and CD are equal and are equally inclined to AD,  $BM = CN$ ; therefore  $\angle BMF = \angle CNE$  and  $\angle BAE = \angle CDE$ . We have, therefore, that  $\theta$  being given, we can construct a hexagon for *any* angle (within certain limits) between the planes ABC, ACD. In other words the hexagon is deformable without altering  $\theta$ .

For the construction of the rigid hexagons, we take a cylinder whose base circumscribes the equilateral triangle BFD with side  $2b$ . If  $\theta > 60^\circ$  but  $< 120^\circ$ , we obtain the hexagon  $A'B'C'DE'F$  by taking points  $A', C', E'$  at a suitable height above the plane DFB on the generators diametrically opposite to D, F, B respectively. If  $\theta > 120^\circ$ , however, we can get another hexagon ABCDEF by taking the points A, C, E at a suitable height on the generators through D, F, B respectively, (fig. 8).

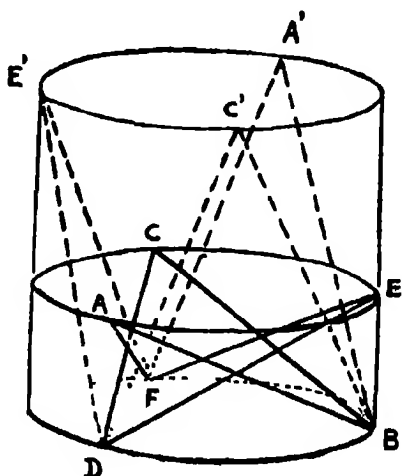


FIG 8

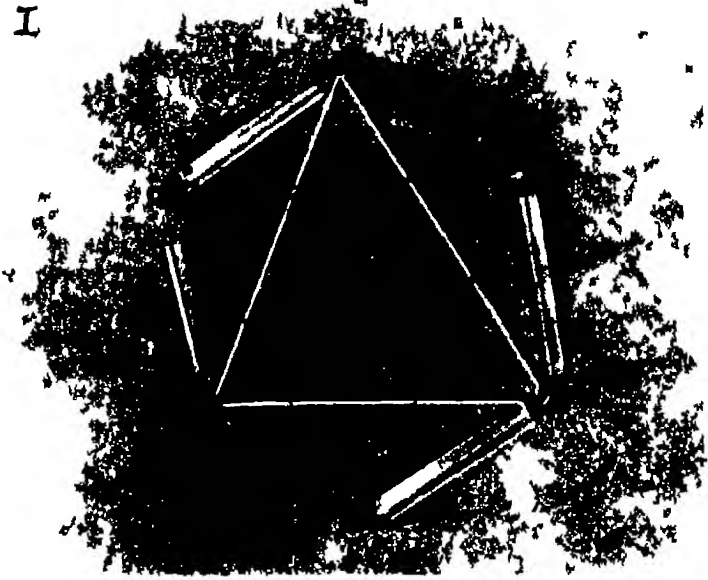
We can also attempt to construct the rigid hexagon by the method of the last paragraph. The two quadrilaterals ABCD, AFED are then equal but not superposable, if ACD and AED are superposed, B and F lie on opposite sides of the plane. If AFED is now rotated through any angle, the arcs BF and CE cannot be equal if measured in the same sense, but they *may* be equal if measured in opposite senses, if AFED is rotated through a suitable angle. For a particular value of  $\theta$ , there are therefore only one or two values of the angle between BCD and ABC which would give the required type of figure.

10. Models to study the properties of these polygons can be very simply constructed by taking a number of equal rigid wires bent in the middle at the required angle. If the ends of these are passed through close-fitting capillary tubes of suitable length, we can construct these polygons mechanically. Two such polygons are shown in plates I and II. I shows the rigid type of hexagon while II shows the flexible type. The diagonal triangles are shown by strings of different colours.

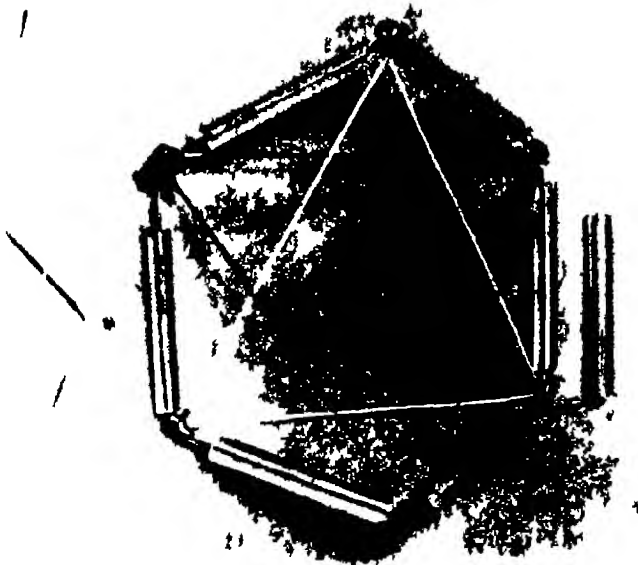
11. Polygons of more than six sides are not studied here as the degrees of freedom increase rapidly with the number of sides. For

PLAIF I

I



PLAIL II





*plane* polygons of many sides, a reference may be made to a paper by Drew in the Journal of Chemistry and Industry of 30th June 1933.

In conclusion, I have to thank Dr. T. S. Wheeler for suggesting this investigation and Messrs. Dalal, Senior and Junior and Mr. Joglekar for help in making models and charts. I have also to thank Dr. S. Brodetsky for supplying me with a reprint of his paper.

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## THE REGULAR CONCAVE POLYHEDRA

By Prof P. K. KASHIKAR, M. A.

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A polyhedron is said to be concave, when the whole of it does not lie on the same side of any face, and a concave polyhedron is said to be regular when all its bounding polygons are congruent and regular, all the dihedral angles (along the edges) are equal, and all the polyhedral angles have the same number of faces.

Cauchy has proved in one of his papers—"Recherches sur les polyedres" (Cauchy's Papers, second series, Vol. I) that if such figures exist then the innermost polyhedron enclosed by the faces must be regular and convex; and then by examining the five convex solids Cauchy proves that only four such figures exist. But the method used by Cauchy in this part of the investigation does not give a clear idea of the solid angles of these figures although it determines the form of the bounding polygons. The alternative method given in the present paper determines the number and form of the solid angles as well as of the bounding polygons of each solid and thus gives some idea of the whole figure.

Cauchy's first result that the concave figures can be obtained from the five convex solids by producing their faces until they meet in a point or a line will be assumed. Also the following theorem which can be easily proved.

**Theorem** If any concave polygon—plane or spherical—which does not consist of two or more smaller interlacing polygons, has all its sides equal and also all its angles equal, then the vertices are symmetrically arranged on the circumference of a circle and the innermost figure enclosed by the sides is a regular convex polygon. With the help of this theorem it can be shown by the method of spherical projection that if any polyhedral angle—convex or concave—has all its plane angles equal and also all its dihedral angles equal then the faces touch a circular cone, the edges lie on another coaxial circular cone, and the faces and the edges are symmetrically arranged round the axis. Such a polyhedral angle may be said to be regular and the axis of symmetry may be called the axis of the regular polyhedral angle.

It is easy to see that all the polyhedral angles of a concave regular solid are regular, and congruent with one another.

Now by Cauchy's theorem the innermost polyhedron enclosed by the plane faces of a concave regular solid is convex and regular and hence the concave solid must have an inscribed sphere. Also by definition all the edges are equal; the bounding polygons are regular and congruent and all the dihedral angles are equal. Reciprocating with respect to the inscribed sphere and remembering that the reciprocal of a regular polyhedral angle in this case is a regular polygon (convex or concave according as the polyhedral angle is convex or concave) we see that in the reciprocal figure all the dihedral angles will be equal, all the polyhedral angles will be regular and congruent, all the edges will be equal and the vertices will coincide with those of a regular convex solid. It follows that all the bounding polygons must be regular and congruent. Hence the reciprocal figure must be a concave regular polyhedron. We have thus proved that the vertices of all such solids coincide with the vertices of some regular convex solid, the edges of the concave figure coinciding with the edges or the diagonals of the convex figure.\* Also the edges at any vertex must be equal, and must make the same angle with the central radius to that vertex. Hence to find the possible types of the concave regular solids we may take a vertex  $P$  of one of the 5 convex solids and find the systems of possible edges meeting at  $P$ .

In examining the five solids for this purpose it will be found convenient to represent the corners surrounding  $P$  by points in a plane perpendicular to the central radius  $OP$ , the distances from  $P$  remaining unaltered. The solid is supposed to be held with the vertex  $P$  turned towards the observer. The vertex opposite to  $P$  is not shown in the figure.

$A_1$   
 $\bullet$   
 $\bullet P$   
 $A_2$        $A_3$

I. In the tetrahedron there is only one system of lines meeting at  $P$ , and thus gives the solid angle  $P (A_1 A_2 A_3)$  which belongs to the tetrahedron

$B_1$

II. In the cube there are 2 systems of lines at  $P$ .

$A_3$        $A_2$  (1)  $PA_1, PA_2, PA_3$  these give the solid angle  
 $\bullet$        $P (A_1 A_2 A_3)$  of the cube  
 $\bullet P$

$B_2$        $A_1$        $B_3$  (2)  $PB_1, PB_2, PB_3$  these are the edges of a  
 $\bullet$                 solid angle belonging to a tetrahedron  
and the complete figure obtained by drawing such lines at all the

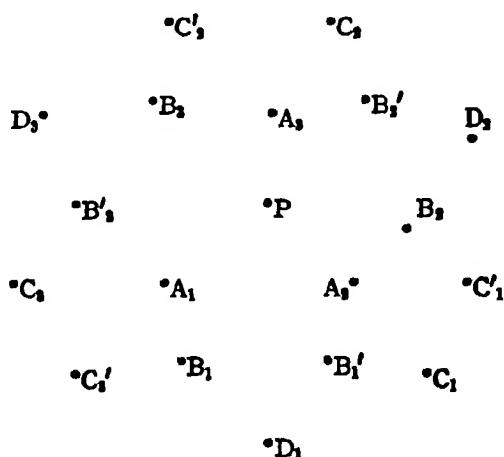
\* This may also be proved directly by the method used in Cauchy's paper.



vertices consists of two interesting tetrahedra. This figure can also be obtained by stellating the octahedron.

°A<sub>3</sub> III. In the octahedron there is only one  
 A<sub>4</sub>° °P °A<sub>2</sub> system and the corresponding solid angle P  
 (A<sub>1</sub>A<sub>2</sub>A<sub>3</sub>A<sub>4</sub>) belongs to the octahedron.  
 °A<sub>1</sub>

IV. In the dodecahedron we get six systems of lines and the corresponding solid angles are



(1) P (A<sub>1</sub>A<sub>2</sub>A<sub>3</sub>) This belongs to the dodecahedron.

(2) P (B<sub>1</sub>B<sub>2</sub>B<sub>3</sub>, B<sub>1</sub>'B<sub>2</sub>'B<sub>3</sub>') This consists of two solid angles P (B<sub>1</sub>B<sub>2</sub>B<sub>3</sub>) and P (B<sub>1</sub>'B<sub>2</sub>'B<sub>3</sub>') each of which belongs to a cube and the whole figure obtained by drawing such lines at all the vertices, consists of five interesting cubes.

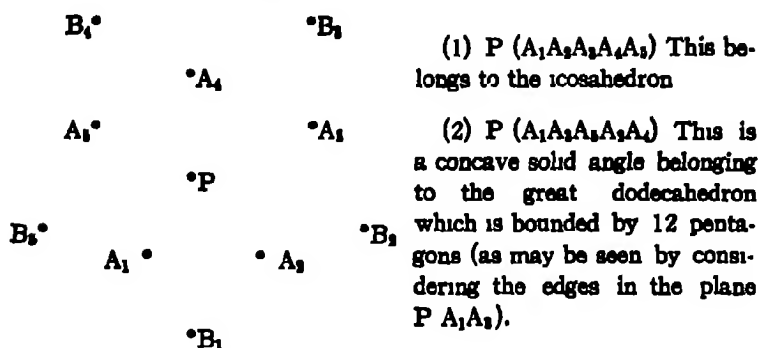
(3) P (C<sub>1</sub>C<sub>2</sub>C<sub>3</sub>) This belongs to a tetrahedron, and the whole figure consists of five intersecting tetrahedra. The twenty vertices belong to a dodecahedron and the twenty faces enclose an icosahedron

(4) P (C<sub>1</sub>'C<sub>2</sub>'C<sub>3</sub>') This also belongs to a tetrahedron and the whole figure is the mirror image of the figure in (3).

(5) P (C<sub>1</sub>C<sub>2</sub>C<sub>3</sub>, C<sub>1</sub>'C<sub>2</sub>'C<sub>3</sub>') This solid angle belongs to the combined system of 10 tetrahedra [(3) + (4)].

(6) P (D<sub>1</sub>D<sub>2</sub>D<sub>3</sub>) This trihedral angle belongs to the concave solid, called the great stellated dodecahedron. Considering the edges in the plane PD<sub>1</sub>D<sub>2</sub>, we see that each bounding polygon is a concave pentagon. Also the plane P D<sub>1</sub>D<sub>2</sub>, is parallel to a face of the dodecahedron. Hence there are 12 such planes and therefore the concave figure is bounded by 12 concave pentagons.

V. In the icosahedron there are two systems of lines at P, each of which gives 2 solid angles.



(3) P ( $B_1 B_2 B_3 B_4 B_5$ ) This convex solid angle belongs to the small stellated dodecahedron which is bounded by 12 concave pentagons (consider the edges in the plane P  $B_1 B_5$ ).

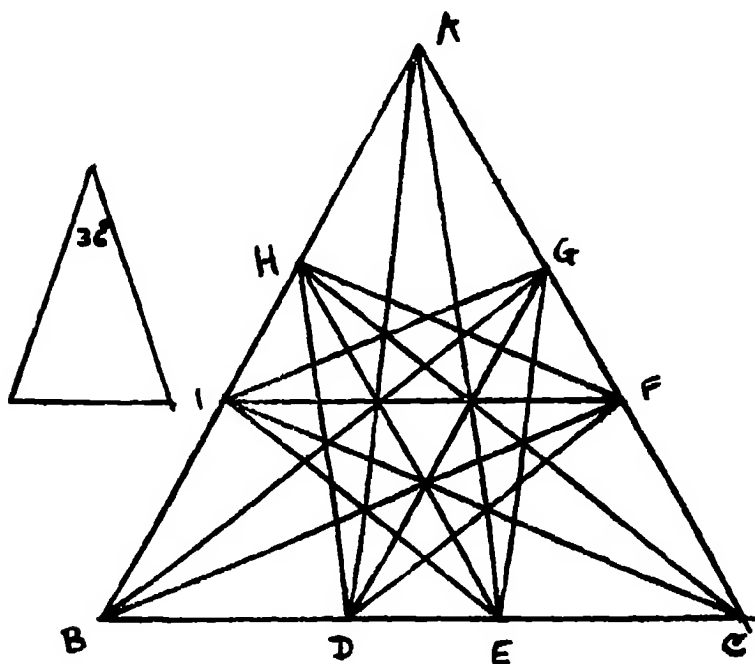
(4) P ( $B_1 B_2 B_3 B_4 B_5$ ) This concave solid angle belongs to the great icosahedron which is bounded by 20 equilateral triangles (consider the edges in the plane P  $B_1 B_5$ ).

Thus we get only four concave regular polyhedra, when the symmetrical combinations of the convex solids are excluded. It is not difficult to prove that, of these four solids the great dodecahedron is the reciprocal of the small stellated dodecahedron, and the great icosahedron is the reciprocal of the great stellated dodecahedron.

It has been stated above that these concave figures can be obtained from the convex solids, by producing their faces until they meet in a point or a line, but this gives some other figures also, which are not regular but are bounded by congruent polygons. From the octahedron we get only one figure which consists of 2 intersecting tetrahedra. Three figures (1) the small stellated dodecahedron (2) the great dodecahedron and (3) the great stellated dodecahedron—can be obtained from the dodecahedron by repeated stellation, and all of these are regular. From the icosahedron it is possible to obtain 19 figures only one of which—the great icosahedron—is regular. Some of these other figures are very interesting. The figure obtained after the 2nd stellation consist of 5 intersecting octahedra, and after the 5th stellation we get 3 figures two of which consist of 5 intersecting tetrahedra and are mirror images of one another, and the third consists of 10 intersecting tetrahedra.

It is easy to construct string models of these figures by first constructing stick—or wire—models of the dodecahedron and icosahedron and then joining the proper vertices by strings which will form the edges of the concave solid.

For constructing cardboard models however it is necessary to determine all the plane angles of the figure to be constructed. This can be easily done in the case of the 3 figures obtained from the dodecahedron, but in the case of the stellated icosahedra the following method must be used. If we take any face  $F$  of the icosahedron, then the other faces when produced will meet  $F$  in st. lines forming a certain rectilinear figure, and this figure will have some more lines added to it after each stellation of the solid. Hence if  $\alpha$  and  $\beta$  are two icosahedra such that  $\beta$  is obtained from  $\alpha$  by a number of stellations, then the figure on a face of  $\alpha$  will form a part of the figure on a face of  $\beta$ . Now the great icosahedron happens to be the last but one figure in the series of stellated icosahedra and the figure on its face is an equilateral triangle crossed by certain other st. lines shown in the accompanying figure (which is interesting by itself owing to the large number of groups of concurrent st. lines and collinear points).



BD, DE, EC are taken equal to the sides of an isosceles triangle whose base is DE and vertical angle  $36^\circ$ . ABC is an equilateral triangle.  $BD = BI = AH = AG = CF = CE$ . The points are joined as shown in the figure. If the sides of the 3 triangles ABC, DFH and EGI be produced to meet one another we get the net of lines on a face of the last figure in the series. All the plane angles occurring in any stellated icosahedron, can now be obtained by identifying its bounding

polygon with a part of this figure and using the methods of Plane Trigonometry to calculate the angles.

Coloured cardboard models of all these figures, constructed by the present writer, have been placed in the Wilson College Library.

Beautiful photographs of these and several other figures will be found in a German book—'Vielecke und Vielflach' by Brückner which contains a large number of theorems, about different kinds of polygons and polyhedra, and many historical notes. For further information the reader is referred to this book, where he will also find other references.

# THE CLASSIFICATION OF INTEGERS

By D D KOSAMBI

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In dealing with number-theoretic operations, we find certain operators extensible to continuous variables, and some for which no immediate extension is to be seen from natural numbers to the continuum. Here, I consider an operator of the latter type, and show its uses in classifying the entire scheme of positive integers. This note also propounds a problem, or rather many related problems without giving explicit solutions. In some cases, a good deal has been discovered about the answers, whereas the expert technician will have no difficulty in recognizing that the rest are practically insoluble in our present state of knowledge regarding the theory of numbers

1. For any positive integer  $n$ , we define the operator

$K[n]$  = The sum off all factors of  $n$  including unity, but excluding  $n$  itself.

Thus.  $K[1] = 0$   $K[2] = K[3] = K[p] = 1$   $p$  any prime.  
 $K[2^r] = 2^r - 1$  etc.

A first classification of the numbers can be effected into.

abundant numbers  $K[n] > n$

deficient numbers.  $K[n] < n$

and the boundary class, usually included with the abundant, of the perfect numbers  $K[n] = n$ . The problem of the distribution, or rather the proportion of these, has been attacked with some success, with the knowledge that the deficient numbers form slightly more than a half of the total. As the multiples of any abundant or perfect number are also abundant, a more essential problem is the number of *primitive* abundant numbers, one to which Dickson has made several most brilliant contributions

It is seen that  $K[n] = m$  regarded as an equation for  $n$ , given  $m$ , has not always a solution, as for example,  $m = 2, 5, \dots$ . Again, the solution whenever it exists, need not be unique.

2. The operator  $K[n]$  may be repeated.

$K[K[n]] = K^2[n]$  and so on.

If  $K^r[n] = 1$  then  $r$  is defined as the *class* of the integer  $n$ . The class of unity will be defined as zero from the outset, and it will then be the only number in its class. Whereas every integer has

another derived from it by the application of the operator  $K$ , not every integer has a class. For instance

The perfect numbers  $K[n] = n$

The amicable numbers  $K[n] = m \quad K[m] = n$

We shall call numbers of this type cyclic numbers, the cycle being the least value of  $s$  for which

$$K^s [n] = n$$

holds true. The members of the cycle are then given by

$$K[n] \quad K^2[n] \quad K^3[n] \dots K^{s-1}[n]$$

I do not recall having seen any discussion of numbers of cycle greater than two.

There is still a further possibility of numbers without class. the numbers of class or cycle infinity. By this is meant numbers  $n$ , if any, such that for every  $a$ , another  $b$  exists to satisfy the inequality.

$$K^a [n] < K^b [n]$$

3. The problems arising out of this classification may be viewed *en bloc*:

1. What is the nature and distribution of the integers  $m$  which cannot be derived by an operation, *i. e.*, for which there is no  $n$  satisfying

$$K[n] = m$$

2. When are the solutions of the above equation unique, and what is the maximum number of solutions possible for such an equation?

3. Are there numbers in every class, and how many? For instance, primes are integers of class one, and known to be infinite in number. Here, we query whether

$$K^r [n] = 1$$

has any solutions for a given  $r$  and the number of these.

4. Do there exist numbers of any preassigned cycle: are there solutions for every  $s$  of

$$K^s [n] = n$$

and how many sets?

The questions 3 and 4 concern the existence and number of solutions of simple operational equations; the general problem is too vague to be of interest at present.

5. Are there numbers without class or cycle?

6. Are there integers of mixed class and cycle? *i. e.*, integers which, after a certain number of operations, reduce to a cyclic number. [These can be shown to exist, as for example  $K[25] = 6$ ,  $K[6] = 6$ . This also shows the non-uniqueness of the solutions of operational]

equations]. Are there integers of the mixed type for every class and every possible cycle? And what is their distribution?

7. The integers being written down in their order, what is the distribution into classes and cycles? In the set

$$1, 2, 3, 4, 5, 6, \dots, N.$$

how many classes and cycles are there represented, and what is the number of integers in each class and cycle represented, under the limit  $N$ ? How many mixed integers are there under the limit?

It should be noted that this is a generalization of the classical problem regarding the distribution of primes. It may be hoped that the two supplement each other, and that some light will be thrown in the near future on the more general problem as related to the older one. As stated, this may be called the problem of the classification of integers.

# THE RESISTANCE OF A SPHERE DUE TO ITS UNIFORM TRANSLATION IN A VISCOUS LIQUID

By D K SEN

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It has been demonstrated by experimental investigations<sup>1</sup> and by theoretical considerations<sup>2</sup> as well, that Stokes's law can only give a rough value for the resistance experienced by a sphere as it moves uniformly in a viscous liquid. The main object of the present paper has been to determine an expression for the resistance which would have a larger domain of validity than Stokes's formula. It may be remarked that the formula obtained in this paper has its limitations but it is believed that the range of its applicability is larger than that of any other corrected form of Stokes's law. An attempt has also been made here to suggest an approximate form of the *complete* equations of motion, which would be valid at infinity.<sup>3</sup>

## 1. General Transformation

Suppose the sphere to be moving with a uniform velocity  $U$  in a direction which we take as the axis of  $x$ . Since the motion is taken to be steady the complete equations of motion referred to a system of parallel axes moving with and through the centre of the sphere, are

$$\left. \begin{aligned} & \frac{1}{\nu} \left[ (u - U) \frac{\partial u}{\partial x} + v \frac{\partial u}{\partial y} + w \frac{\partial u}{\partial z} \right] - \frac{X}{\nu} - \frac{1}{\mu} \frac{\partial p}{\partial x} + \nabla^2 u, \\ & \frac{1}{\nu} \left[ (u - U) \frac{\partial v}{\partial x} + v \frac{\partial v}{\partial y} + w \frac{\partial v}{\partial z} \right] - \frac{Y}{\nu} - \frac{1}{\mu} \frac{\partial p}{\partial y} + \nabla^2 v, \\ \text{and } & \frac{1}{\nu} \left[ (u - U) \frac{\partial w}{\partial x} + v \frac{\partial w}{\partial y} + w \frac{\partial w}{\partial z} \right] - \frac{Z}{\nu} - \frac{1}{\mu} \frac{\partial p}{\partial z} + \nabla^2 w, \end{aligned} \right\} \dots (1)$$

$$\text{together with} \quad \frac{\partial u}{\partial x} + \frac{\partial v}{\partial y} + \frac{\partial w}{\partial z} = 0, \quad (2)$$

where  $u, v, w$  are the components of the velocity and  $p$  the pressure at any point in the liquid whose co-ordinates are  $(x, y, z)$  referred to

1. H. S. Allen, *Phil. Mag.*, 1900, pp 323-338, H. D. Arnold, *Phil. Mag.*, 1911, Vol. 22.

2. C. W. Oseen, *Arkiv f. Mat. Astro. och Fys.*, Bd 6, 1911, H. Lamb, *Phil. Mag.*, Vol. 21, 1911, R. W. Burgess, *Amer Jour of Math.*, Vol. 38, 1916. Also see Lamb's *Hydrodynamics*, 5th Edition.

3. I would like to express my thanks to Dr. Ganesh Prasad and to Prof C. W. Oseen and Dr. H. Faxen (of the University of Upsala, Sweden) for their kind and valuable criticisms and suggestions during the preparation of this work.



the moving axes,  $\nu$  ( $=\mu/\text{density}$ ) the kinematic co-efficient of viscosity, and  $X, Y, Z$  the components of extraneous forces. Since the vortex lines must be circles having the axis of  $x$  as the common axis, we may assume

$$\xi = 0, \eta = -\frac{\partial \chi}{\partial z}, \zeta = \frac{\partial \chi}{\partial y}, \quad (3)$$

where  $\chi$  is a function of  $x$  and  $\omega$  ( $=\sqrt{y^2+z^2}$ ) only, and

$$\xi = \frac{\partial \omega}{\partial y} - \frac{\partial v}{\partial z}, \eta = \frac{\partial u}{\partial z} - \frac{\partial w}{\partial x}, \zeta = \frac{\partial v}{\partial x} - \frac{\partial u}{\partial y}. \quad (4)$$

From (3) we get  $\frac{\partial \omega}{\partial y} = \frac{\partial v}{\partial z}$ , and so we further assume

$$v = \frac{\partial^2 f}{\partial x \partial y} \text{ and } w = \frac{\partial^2 f}{\partial x \partial z}, \quad (5)$$

$f$  being, like  $\chi$ , a function of  $x$  and  $\omega$ . We then get, from the other equations of (3),

$$\begin{aligned} \frac{\partial u}{\partial z} - \frac{\partial^2 f}{\partial x^2 \partial z} &= -\frac{\partial \chi}{\partial z} \\ \text{and} \quad \frac{\partial u}{\partial y} - \frac{\partial^2 f}{\partial x^2 \partial y} &= -\frac{\partial \chi}{\partial y}, \end{aligned}$$

which are obviously satisfied by

$$u = \frac{\partial^2 f}{\partial x^2} - \chi. \quad (6)$$

The equation (2) then gives

$$-\frac{\partial \chi}{\partial x} + \frac{\partial^2 f}{\partial x^3} + \frac{\partial^2 f}{\partial x \partial y^2} + \frac{\partial^2 f}{\partial x \partial z^2} = 0;$$

$$\text{whence we have } \chi = \nabla^2 f. \quad (7)$$

Thus  $u, v, w$  are expressed in terms of a single function  $f$  which contains as we know,  $x$  and  $\omega$  only. This may be further simplified by assuming that  $f$  is a function of  $x$  and  $\rho$  ( $=\sqrt{x^2+\omega^2}$ ). It may be noticed that this function is tacitly taken to be continuous and its derivatives, upto a certain order, to be existent.

If the extraneous forces have a potential, we can obtain from (1), by cross-differentiation, the following.

$$\frac{1}{\nu} \left[ (u-U) \frac{\partial}{\partial x} + v \frac{\partial}{\partial y} + w \frac{\partial}{\partial z} - \frac{\nu}{y} \right] \frac{\partial \chi}{\partial y} = \nabla^2 \left( \frac{\partial \chi}{\partial y} \right). \quad (8)$$

This then is the equation from which the function  $f$  is to be determined.

## 2. *Objections to the Previous Results.*

Stokes's results could be obtained from (8) if the left-hand side be neglected altogether; that is, if we take

$$\nabla^2 \left( \frac{\partial \chi}{\partial y} \right) = 0 \text{ or } \nabla^2 \chi = 0, \quad (9)$$

instead of (8), as our fundamental equation. The solution of  $-\frac{\partial \chi}{\partial y} = 0$  is neglected for obvious reasons. The simplest solution of (9), compatible with the condition of rest at infinity, is

$$\chi = \frac{c}{\rho} \quad \text{or} \quad \nabla^2 \chi = \frac{c}{\rho}.$$

Taking  $f$  to be a function of  $\rho$ , we get

$$\rho^3 \frac{d^2 f}{d\rho^2} + 2\rho \frac{df}{d\rho} = c\rho,$$

whence

$$f = \frac{d}{\rho} + \frac{1}{2} c\rho;$$

$$\left. \begin{aligned} \text{leading to } u &= -\frac{c}{2\rho} - \frac{d}{\rho^3} + \left( \frac{d}{\rho^3} - \frac{c}{2\rho^3} \right) x^2, \\ v &= \left( \frac{d}{\rho^3} - \frac{c}{2\rho^3} \right) xy \text{ and } w = \left( \frac{d}{\rho^3} - \frac{c}{2\rho^3} \right) xz. \end{aligned} \right\} \quad (10)$$

The condition of non-slipping at the surface of the sphere ( $\rho = a$ ) requires that

$$c = -\frac{3}{2} Ua, \quad d = -\frac{1}{2} Ua^3. \quad (11)$$

Prof. Oseen<sup>1</sup> has shown that although this solution of Stokes holds for points near the sphere, it is not valid at points at great distance from the latter. The reason advanced by him is that the ratio of the hypothetical constraining forces to the viscous forces is of the order  $U\rho/\nu$  which becomes infinite with  $\rho$ ; hence it would not be justifiable to omit altogether the terms on the left-hand sides of the equations of motion for the region far removed from the sphere. The modified solution given by him satisfies the equation (8) when all the terms on the left-hand side, excepting the one involving  $U$ , are omitted.

This modified equation, which we may name (8 A), can also be obtained from the following considerations.<sup>2</sup> Consider the term  $(u-U) \frac{\partial u}{\partial x}$ ; at points very near the sphere  $(u-U)$  is quite small and hence the neglect of this term may be justified here. But at distant points  $(u-U)$  is not small; in fact, it tends to  $-U$  as we recede farther and farther from the sphere. Therefore for the region far removed from the sphere the equation can take the approximate form (8 A).

Now as the value of  $u$  ranges from  $U$  to zero, it is obvious that there are points at which  $(u-U)$  neither assumes a value negligibly small nor a value which differs from  $-U$  by a very small quantity;

1. Loc. cit.

2. Cf. Burgess and Oseen, loc. cit.

its value at these points can rather be denoted by  $\bar{u} - U\lambda$ , where  $\lambda$  is a proper fraction, and the equations of motion have here to be suitably modified. The form (8A) does not hold here.

Again, the equation (8A) can be obtained from (1) by omitting terms  $u \frac{\partial u}{\partial x}$ , . . . from the left hand sides. As  $u$  has values ranging from  $U$  to zero, it would not be reasonable to take terms like  $-U \frac{\partial u}{\partial x}$  into account whilst neglecting terms of the same order of magnitude (for some points at least), viz  $u \frac{\partial u}{\partial x}$ , etc.

Thus we see that while the equations Stokes started from are true for points very near the sphere and those considered by Prof Oseen (and also by Prof Lamb) for points far from the sphere, no provision has been made for the intermediate region. Prof Lamb has, however, shown that the latter results can, to a first approximation, be applicable to this region also. In order to include this domain into our considerations we must take the *complete* equations of motion.

### 3 Consideration of the complete equations of motion

We have seen that the complete equations of motion (1) can be reduced to a single equation (8) involving only one unknown function  $f$ . This equation cannot, however, be solved completely, but it is possible to obtain approximate solutions by a process of successive approximation. We shall put  $k = U/2\nu$ , as has been done by Prof Lamb.

As  $f_0$ , where  $\nabla^2 f_0 = 0$ , also furnishes a solution for  $f$  we can put

$$u = u_0 + u', \quad v = v_0 + v' \quad \text{and} \quad w = w_0 + w' \quad (12)$$

for our complete solution,  $u_0, v_0, w_0$  being derivable from  $f_0$ . The condition of rest at infinity requires that

$$\left. \begin{aligned} u_0 &= c_0 \frac{\partial}{\partial x} \left( \frac{1}{\rho} \right) + c_1 \frac{\partial^2}{\partial x^2} \left( \frac{1}{\rho} \right) + \\ v_0 &= c_0 \frac{\partial}{\partial y} \left( \frac{1}{\rho} \right) + c_1 \frac{\partial^2}{\partial x \partial y} \left( \frac{1}{\rho} \right) + \\ w_0 &= c_0 \frac{\partial}{\partial z} \left( \frac{1}{\rho} \right) + c_1 \frac{\partial^2}{\partial x \partial z} \left( \frac{1}{\rho} \right) + \end{aligned} \right\} \quad (13)$$

We propose now to obtain approximate solutions of (8) in the case of slow motion, that is, when  $ka$  is a small quantity. For a first approximation we shall neglect all terms involving second and higher powers of  $ka$ . We assume that  $f = f_1 + f_2$ ,

$$\left. \begin{aligned} \text{where} \quad f_1 &= e^{-k\rho} [A_0 (1 + k\rho) + A_1 x] \\ \text{and} \quad f_2 &= e^{-2k\rho} [B_0 + B_1 x] \end{aligned} \right\} \quad (14)$$

the A's and the B's being functions of  $\rho$  and the B's being dependent on the A's satisfies the equation (8) to the first approximation. For the sake of convenience we shall denote by  $u_1, v_1, w_1, \chi_1$ , the values of  $u, v, w, \chi$ , derived from  $f_1$  and similarly for others. Also, by  $D_n$  the operator

$$\frac{1}{\nu} \left[ u_n \frac{\partial}{\partial x} + v_n \left( \frac{\partial}{\partial y} - \frac{1}{y} \right) + w_n \frac{\partial}{\partial z} \right] \frac{\partial}{\partial y}.$$

We do not purposely take into account such values of  $f$  (except  $f_0$ ) which do not possess  $e^{-k\rho}$  as factor, since it can easily be shown that they furnish velocity-components which are incompatible with the condition of rest at infinity. For the same reason we take it that the unknown functions of  $\rho$ , viz  $A_0$ , etc., do not contain any exponential factor, in other words we shall treat them as polynomials only.

The form of Stokes's solution leads us to assume further that only  $c_1$  and the function  $A_0$  include terms free from  $k$ . The values of these functions can be derived from the equations we would obtain by equating the coefficients of  $e^{-k\rho}$  and  $e^{-2k\rho}$  from the two sides of the equation (8) when the presumed solutions are put in. Substituting (12) and (14) in (8) we thus get to this approximation

$$\left( \nabla^2 + 2k \frac{\partial}{\partial x} \right) \frac{\partial \chi_1}{\partial y} = D_0 \chi_1, \quad (15)$$

$$\text{and} \quad \left( \nabla^2 + 2k \frac{\partial}{\partial x} \right) \frac{\partial \chi_2}{\partial y} = D_0 \chi_2 + D_1 \chi_1. \quad (16)$$

The equation (15) will hold if

$$F_0'' A_0 = 0, \quad (17)$$

$$F_1'' A_1 = \left( -2k + \frac{2c_1}{\nu \rho^3} \right) F_0' A_0, \quad (18)$$

$$\left. \begin{aligned} \text{where} \quad F_n'' &= \frac{d^5}{d\rho^5} + \frac{4(n+1)}{\rho} \frac{d^4}{d\rho^4} + \frac{4(n^2-1)}{\rho^3} \frac{d^3}{d\rho^3} - \frac{12n(n+1)}{\rho^5} \frac{d^2}{d\rho^2} \\ &\quad + \frac{12n(n+1)}{\rho^4} \frac{d}{d\rho} \\ \text{and} \quad F_n' &= \frac{1}{\rho} \frac{d^4}{d\rho^4} + \frac{2n+1}{\rho^3} \frac{d^3}{d\rho^3} - \frac{6(n+1)}{\rho^5} \frac{d^2}{d\rho^2} + \frac{6(n+1)}{\rho^4} \frac{d}{d\rho} \end{aligned} \right\} \quad (19)$$

These equations are satisfied by

$$A_0 = \frac{a_1}{\rho} + a_2 \rho, \quad (20)$$

$$\text{and} \quad A_1 = \frac{a_3}{\rho} + \frac{a_4}{\rho^3} - \frac{1}{2} a_2 k \rho + \frac{a_5 c_1}{4\nu \rho^3}, \quad (21)$$

the  $a$ 's being constants. The equation (16) then gives

$$F_0'' B_0 = 0 \quad (22)$$

and 
$$\rho^3 F_1'' B_1 = \frac{12a_2}{\nu} \left( \frac{a_1}{\rho^3} - a_2 \right); \dots (23)$$

whence  $B_0 = 0$  and  $B_1 = \frac{a_2}{4\nu} \left\{ \frac{a_1}{\rho^3} - 2a_2 \log(k\rho) \right\} \dots (24)$

From the condition of non-slipping at the surface of the sphere we next obtain

$$c_0 = 0, a_1 + c_1 = -\frac{1}{2} U a^3, a^3 = -\frac{1}{2} U a.$$

$$a_3 = -\frac{3}{16} U k a^3, a_4 - c_2 = -\frac{1}{16} U k a_3.$$

Thus we see that we can safely put  $c_0 = c_1 = c_2 = 0$ . Hence the subsequent values of the constants, viz

$$a_1 = -\frac{1}{2} U a^3, a_2 = -\frac{1}{2} U a, a_3 = -\frac{3}{16} U k a^3, a_4 = -\frac{1}{16} U k a^3, (25)$$

lead to

$$u = e^{-k\rho} \left[ (1+k\rho) \left\{ \left( \frac{3}{2} \frac{Ua}{\rho} + \frac{1}{2} \frac{Ua^3}{\rho^3} \right) + x^3 \left( \frac{3}{2} \frac{Ua}{\rho^3} - \frac{3}{2} \frac{Ua^3}{\rho^3} \right) \right\} \right. \\ \left. + \frac{3}{8} \frac{Ukax}{\rho} \left( -1 + \frac{a^3}{2\rho^3} + \frac{3a^4}{2\rho^4} \right) - \frac{3}{8} \frac{Ukax^3}{\rho^3} \left( 1 + \frac{5a^3}{2\rho^3} + \frac{3a^4}{2\rho^4} \right) \right] \\ + e^{-2k\rho} \left[ -\frac{3}{8} \frac{Uka^4x}{\rho^4} + \frac{3}{8} \left( 3 + \frac{2a^3}{\rho^3} \right) \frac{Uka^3x^3}{\rho^4} \right], (26)$$

$$v = e^{-k\rho} \left[ (1+k\rho) \left( \frac{3}{2} \frac{Ua}{\rho^3} - \frac{3}{2} \frac{Ua^3}{\rho^3} \right) xy + \frac{3}{8} \frac{Ukxy}{\rho} \left( 1 + \frac{a^3}{2\rho^3} + \frac{a^4}{2\rho^4} \right) \right. \\ \left. - \frac{3}{8} \frac{Ukx^3y}{\rho^3} \left( 1 + \frac{5a^3}{2\rho^3} + \frac{3a^4}{2\rho^4} \right) \right] \\ + e^{-2k\rho} \left[ -\frac{9}{16} \left( 1 + \frac{a^3}{3\rho^3} \right) \frac{Uka^3y}{\rho^3} + \frac{3}{8} \left( 3 + \frac{2a^3}{\rho^3} \right) \frac{Uka^3x^3y}{\rho^4} \right], (27)$$

and similarly for  $w$ .

#### 4. The second approximation.

We next carry the calculations to the second degree of approximation by retaining terms involving the second power of  $ka$ . We begin by assuming our solution to be

$$f = f_1 + f_2 + f_3 \dots (28)$$

where  $f_1 = e^{-k\rho} \left[ \left( \frac{a_1}{\rho} + a_2 \rho \right) + \left( \frac{a_3}{\rho} + \frac{a_4}{\rho^3} - \frac{1}{2} a_2 k \rho \right) x + A_0 + A_1 x + A_2 x^2 \right], (29)$

$$f_2 = e^{-2k\rho} \left[ \left\{ \frac{a_1}{\rho^3} - 2a_2 \log(k\rho) \right\} \frac{a_2 x}{4\nu} + B_0 + B_1 x + B_2 x^2 \right] \dots (30)$$

and  $f_3 = e^{-3k\rho} [C_0 + C_1 x + C_2 x^2] \dots (31)$

the A's, the B's and the C's all having  $k^3$  as factor. As before, we take it that the values of the functions B and C depend on those of A's. Following the procedure of the last article we get

$$\left. \begin{aligned} A_0 &= \frac{b_1}{\rho} + b_2 \rho + b_3 \rho^3 - \frac{b_4}{3\rho^3} - \frac{5}{12} U k^2 \alpha \rho^3; \\ A_1 &= \frac{b_4}{\rho} + \frac{b_5}{\rho^3} + b_6 \rho^3 - \frac{1}{16} \frac{U k^2 \alpha^3}{\rho^3}, \\ A_2 &= \frac{b_7}{\rho^3} + \frac{b_8}{\rho^5} - \frac{1}{4} U k^2 \alpha \rho + \frac{3}{32} U k^2 \alpha^3. \end{aligned} \right\} \dots (32)$$

$$\text{also } \left. \begin{aligned} B_0 &= U k^2 \alpha^3 \left[ \frac{9}{40} \rho^3 \log k\rho - \frac{3}{64} \alpha^3 \log k\rho + \frac{3}{256} \frac{\alpha^4}{\rho^3} \right]; \\ B_1 &= U k^2 \alpha^3 \left[ -\frac{9}{8} \rho \log k\rho \right]; \\ B_2 &= U k^2 \alpha^3 \left[ \frac{129}{320} \log k\rho - \frac{3}{16} \frac{\alpha^3}{\rho^3} + \frac{3}{512} \frac{\alpha^4}{\rho^4} \right]. \end{aligned} \right\} (33)$$

$$\text{and } \left. \begin{aligned} C_0 &= U k^2 \alpha^3 \left[ \left( \frac{9}{140} \frac{\alpha^3}{\rho} - \frac{1}{560} \frac{\alpha^3}{\rho^3} \right) \log k\rho - \frac{1}{672} \frac{\alpha^4}{\rho^3} \right]; \\ C_1 &= 0; C_2 = U k^2 \alpha^3 \left[ \frac{27}{64} \frac{\alpha}{\rho} + \left( \frac{3}{70} \frac{\alpha^3}{\rho^3} + \frac{3}{560} \frac{\alpha^3}{\rho^5} \right) \log k\rho \right]. \end{aligned} \right\} (34)$$

The values of the constants satisfying the boundary condition at the surface of the sphere can now be easily found to be

$$\begin{aligned} b_1 &= -\frac{6903}{44800} U k^2 \alpha^3 - \frac{81}{280} U k^2 \alpha^3 \log k\alpha; \\ b_2 &= -\frac{431}{3200} U k^2 \alpha^3 - \frac{27}{40} U k^2 \alpha^3 \log k\alpha; \\ b_3 &= 0; b_4 = -\frac{27}{16} U k^2 \alpha^3, b_5 = \frac{3}{8} U k^2 \alpha^3; b_6 = 0; \\ b_7 &= \frac{351}{8960} U k^2 \alpha^3 - \frac{3}{70} U k^2 \alpha^3 \log k\alpha, \\ b_8 &= \frac{401}{44800} U k^2 \alpha^3 - \frac{3}{560} U k^2 \alpha^3 \log k\alpha. \end{aligned} \quad \dots (35)$$

It may be noted that the values of  $u, v, w$ , thus calculated contain certain terms involving  $\log(k\rho)$  as factor. This makes the corresponding terms assume the indeterminate form  $0 \times \infty$  when  $\rho$  is infinite; this does not, however, impair the condition of rest at infinity since the ultimate limit of each of these terms is zero.

Using the values obtained above we find that, in the absence of extraneous forces, the resistance experienced by the sphere is parallel to the  $x$ -axis and is given by

$$R = -6 \pi \mu U \alpha \left[ 1 + \left\{ \frac{887}{800} + \frac{9}{10} \log k\alpha \right\} k^2 \alpha^2 \right] \quad (36)$$

Thus (36) represents what Stokes's law should be upto this approximation.

The method indicated above can be employed with success to obtain better results, that is, upto higher degrees of approximation,

### 5. Comparison with experimental observations.

In order to find within what limits the formula (36) is applicable I have used the results given by Arnold (*loc. cit.*) in Table II of his paper. Arnold's experiments, however, were carried on with small spheres falling in a liquid contained in a long vertical tube. In deriving the formula (36), on the other hand, we had assumed that the liquid was infinite in extent. In Arnold's experiment the condition of infiniteness is to a certain extent maintained on account of the relatively large size of the cross-section of the fall-tube (in comparison with the radius of the falling sphere) used by him, but the liquid in the tube cannot, in the strict sense, be regarded as infinite. It has been shown by Faxén that the effect of the presence of the walls of the tube is to increase the resistance by a factor whose value depends on  $kr$ , where  $r$  is the radius of the cross-section of the tube, when  $k$  is small enough. The resistance calculated from the formula (36) derived in this paper should, in these cases, be less than the actual resistance experienced by the sphere.

Now if a sphere of radius  $a$  and of material whose density is  $\sigma$  be falling in a liquid of density  $d$  under the action of gravity, the force which accelerates its motion is given by

$$\frac{4}{3} \pi a^3 (\sigma - d) g. \quad \dots \quad (37)$$

In the case of steady motion this force will be just balanced by the resistance of the sphere due to the liquid. Thus we get a criterion for testing the degree of accuracy of the various formulas. I shall also be giving, in the succeeding Table, values computed from the formula of Prof. Oseen, viz.

$$R = -6 \pi \mu U a (1 + \frac{1}{2} ka) \dots \dots \dots (38)$$

Again, since the formulas (36) and (38) refer to the terminal velocity and since in the following computations the values of  $U$  used are taken from the experimental observations which are never greater than the terminal velocities, it should be expected that the values calculated from these formulas would be less than those derived from the formula (37).

The validity of the formula (36) is apparent from the Table if we consider that it gives values sufficiently less than those obtained from (37). Prof. Oseen's formula appears to give more approximate results than (36), even when  $a$  is as large as '0704, for this case  $ka$  is sufficiently large and such agreement leaves a doubt in one's mind as to the validity of his formula for such big values of  $a$  at least. For low values of  $a$ , however, the three formulas agree to a very close approximation.

Proceeding to the next higher approximation, I have calculated the expression for the resistance and have found that it consists of a term of the form

$$-6\pi\mu Ua [a+\beta \log ka] k^3 a^3 \dots \dots (39)$$

in addition to the expression (36). The values of  $\alpha$  and  $\beta$  are 7.49 and 2.54 approximately. It has been found that this term produces no perceptible change in the values given in the Table upto  $\alpha = .0329$ . For the remaining cases the increments are:

.001, .003, .003, .004, .020, .059, .078, .100, .171, .310, .655, .837, .921, .963, 1 195, 1 751, 2 223, 4 087, 5 067

respectively. It may be noticed that, for the last two cases only, this causes the value of the resistance to exceed that in the third column. This discrepancy is, I think, due to the fact that the radii of the spheres in these cases are too great for this approximation, and would disappear if terms of higher orders are brought in.

$\alpha$	$ka$	Resistance calculated from		
		Formula (37)	Formula (36)	Formula (38)
.00651	.0005	.00998	.00972	.00972
.00912	.00132	.0274	.0263	.0263
.0102	.0018	.0384	.0365	.0366
.0104	.00194	.0401	.0387	.0388
.0190	.0114	.248	.227	.229
.0200	.0135	.289	.268	.271
.0208	.0156	.325	.310	.313
.0252	.0257	.579	.511	.521
.0301	.0438	.986	.868	.899
.0310	.0476	1.078	.944	.982
.0329	.0567	1.288	1.123	1.177
.0372	.0798	1.862	1.576	1.683
.0400	.0991	2.315	1.954	2.119
.0403	.101	2.367	1.996	2.168
.0408	.106	2.456	2.079	2.267
.0462	.143	3.567	2.814	3.141
.0497	.177	4.440	3.466	3.981
.0510	.187	4.798	3.668	4.241
.0515	.197	4.940	3.866	4.498
.0538	.220	5.632	4.326	5.103
.0562	.2503	6.420	4.938	5.916
.0594	.294	7.580	5.862	7.151
.0609	.3105	8.169	6.213	7.619
.0613	.317	8.319	6.360	7.813
.0619	.320	8.579	6.429	7.905
.0630	.336	9.044	6.780	8.367
.0644	.365	9.660	7.470	9.266
.0688	.385	10.781	7.953	9.883
.0690	.441	11.883	9.605	11.692
.0704	.467	12.620	10.161	12.560

It may be added here that the radius of the fall-tube was .547, so that one may compare this to the radius of the falling sphere.



# ON THE SET OF POINTS $\frac{\Phi(n)}{n^3}$

By

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I. Let  $\Phi(n)$  denotes the number of "Unkurzbar" fractions  
( the fraction  $\frac{a+b}{n}$  ,  $1 \leq a \leq n$  is called "kurzbar"

$\frac{1 \leq b \leq n$   
if  $(a, b, n) > 1$ , "unkurzbar" if  $(a, b, n) = 1$  )

It is known that

$$\Phi(n) = n^3 \left(1 - \frac{1}{p^3}\right) \left(1 - \frac{1}{q^3}\right) \left(1 - \frac{1}{r^3}\right) \dots$$

if  $n = p^a q^b r^c \dots$  where  $p, q, r, \dots$  are different primes.

It follows that if  $f(n) = \frac{\Phi(n)}{n^3}$  then  $0 < f(n) < 1$

We propose to prove :—

\*Th. (1). Every point of the interval  $\left(\frac{6}{\pi^3}, 1\right)$  is a limiting point  
of the set of points  $f(n)$ .

(a) Let  $p_r$  be the  $r$ th prime then

$$f(p_r) = \frac{\Phi(p_r)}{p_r^3} = \left\{1 - \frac{1}{p_r^3}\right\} \rightarrow 1 \quad \text{as } r \rightarrow \infty$$

$\therefore 1$  is a Limiting point of the set of points  $f(n)$ .

(b) Let  $n_r = p_1 p_2 \dots p_r$ . Then

$$f(n_r) = \left\{1 - \frac{1}{p_1^3}\right\} \left\{1 - \frac{1}{p_2^3}\right\} \dots \left\{1 - \frac{1}{p_r^3}\right\}$$

This product tends to  $\frac{1}{\zeta(3)} = \frac{6}{\pi^3}$  as  $r \rightarrow \infty$ ,

Where  $\zeta(s)$  denotes the Zeta Function of Riemann.

$\therefore \frac{6}{\pi^3}$  is a limiting point of the set.

(c) Let  $\frac{6}{\pi^3} < p < 1$   $0 < \epsilon < p - \frac{6}{\pi^3}$

\* For a similar method applied in a different problem, see a paper by  
Dr. T. Vijayaraghavan, I. M. S. Journal, Vol. XII, p. 98.

We prove that a number  $N$  exists such that  $p-\epsilon < f(N) < p$  (1) from which it will follow that  $p$  is a limiting point of the set  $f(n)$ .

Choose a prime number  $P_1$  so large that

$$P_1^2 > \frac{1}{1-p} \quad P_1^2 > \frac{p}{\epsilon} \quad \dots \quad \dots \quad \dots \quad (2)$$

Let  $P_2, P_3, \dots$  be the prime numbers in order following  $P_1$ . Consider numbers  $N_1, N_2, \dots$  defined by

$$N_m = P_1 P_2 \dots P_m \quad (m = 1, 2, \dots)$$

$$\text{Then } f(N_m) = \left(1 - \frac{1}{P_1^2}\right) \left(1 - \frac{1}{P_2^2}\right) \dots \left(1 - \frac{1}{P_m^2}\right)$$

Also  $f(N_1), f(N_2), \dots$  form a decreasing sequence.

$$\text{Further } f(N_1) = 1 - \frac{1}{P_1^2} > 1 - (1-p) = p \text{ from (2).}$$

$\therefore$  If none of the numbers  $N_2, N_3, \dots$  satisfy inequalities (1), there should exist an integer  $k > 1$  so that

$$f(N^k) > p \quad \dots \quad f(N_{k+1}) < p - \epsilon$$

In this case we have

$$\begin{aligned} \left(1 - \frac{1}{P_1^2}\right) \dots \left(1 - \frac{1}{P_k^2}\right) &> p \\ \left(1 - \frac{1}{P_1^2}\right) \dots \left(1 - \frac{1}{P_{k+1}^2}\right) &< p - \epsilon \\ \therefore 1 - \frac{1}{P_{k+1}^2} &< \frac{p - \epsilon}{p} \end{aligned}$$

$$\therefore P_{k+1}^2 < \frac{p}{\epsilon}$$

But  $P_{k+1} > P_1$

$$\therefore P_1^2 < \frac{p}{\epsilon}$$

which contradicts second of inequalities (2). Hence a number  $N$  exists which satisfies (1) and the theorem is therefore proved.

2. Let  $\overline{W}(n)$  = number of "kurzbar" fractions

$$\text{Then } \overline{W}(n) = n^2 - n^2 \left(1 - \frac{1}{p^2}\right) \left(1 - \frac{1}{q^2}\right) \dots$$

$$\therefore \frac{\overline{W}(n)}{n^2} = 1 - \left(1 - \frac{1}{p^2}\right) \left(1 - \frac{1}{q^2}\right) \dots$$

$$\therefore \lim_{n \rightarrow \infty} \frac{\overline{W}(n)}{n^2} = 1 - \frac{6}{\pi^2}$$

$$\lim_{n \rightarrow \infty} \frac{\overline{W}(n)}{n^2} = 0$$

and by Th. (1) we get the result that every point of the interval  $\left(0, 1 - \frac{6}{\pi^2}\right)$  is a limiting point of the set of points  $\frac{\overline{W}(n)}{n^2}$ .

3. Let  $\alpha_n = \frac{\Phi(n)}{n^2}$

Then  $\sum_{n=1}^{\infty} \frac{a_n}{n^s} = F(s)$  is convergent for  $\sigma > 1$  where  $s = \sigma + it$ .

Hence by a well-known Theorem (Landau Primzahlen Vol. I Page 115) we get

$$\overline{\lim}_{s=1} (s-1) f(s) \leq \overline{\lim}_{N=\infty} \frac{\sum_{n=1}^N a_n}{N}$$

$$\underline{\lim}_{s=1} (s-1) f(s) \geq \underline{\lim}_{N=\infty} \frac{\sum_{n=1}^N a_n}{N}$$

$$\text{Now } \sum_{n=1}^{\infty} \frac{a_n}{n^s} = \frac{\zeta(s)}{\zeta(s+2)}$$

$$\text{and } \lim_{s=1} (s-1) \frac{\zeta(s)}{\zeta(s+2)} = \frac{1}{\zeta(3)}$$

$$\therefore \text{ We have } \underline{\lim}_{N=\infty} \frac{\sum_{n=1}^N \frac{\Phi(n)}{n^3}}{N} \leq \frac{1}{\zeta(3)}.$$

$$\overline{\lim}_{N=\infty} \frac{\sum_{n=1}^N \frac{\Phi(n)}{n^3}}{N} \geq \frac{1}{\zeta(3)}.$$

We prove, below, that

$$\underline{\lim}_{N=\infty} \frac{\sum_{n=1}^N \frac{\Phi(n)}{n^3}}{N} = \frac{1}{\zeta(3)}$$

4 Let  $\alpha$  be any real number

Th (2)

$$(a) \sum_{n=1}^N \frac{\Phi(n)}{n^\alpha} = O(1) \quad \text{if } \alpha > 3$$

$$(b) \sum_{n=1}^N \frac{\Phi(n)}{n^\alpha} = \frac{\log N}{\zeta(3)} + O(1) \quad \text{if } \alpha = 3$$

$$(c) \sum_{n=1}^N \frac{\Phi(n)}{n^\alpha} = \frac{N^{3-\alpha}}{(3-\alpha)\zeta(3)} + o(N^{3-\alpha}) \quad \text{if } \alpha < 3$$

Proof

(a)  $\alpha > 3$

$$\sum_{n=1}^N \frac{\Phi(n)}{n^\alpha} < \sum_{n=1}^N \frac{1}{n^{\alpha-2}} < \sum_{n=1}^{\infty} \frac{1}{n^{\alpha-2}} = O(1)$$

(b)  $\alpha = 3$ We have  $\sum_{d|n} \Phi(d) = n^2$ 

$$\therefore \Phi(n) = \sum_{d|n} \mu(d) \frac{n^2}{d^2} = n^2 \sum_{d|n} \frac{\mu(d)}{d^2}$$

$$\begin{aligned} \therefore \sum_{n=1}^N \frac{\Phi(n)}{n^3} &= \sum_{n=1}^N \frac{n^2 - \alpha}{n^3} \sum_{d|n} \frac{\mu(d)}{d^2} \\ &= \sum_{d=1}^N \frac{1}{d^2} \sum_{m=1}^{N/d} m^{2-\alpha} \frac{\mu(d)}{d^2} \\ &= \sum_{d=1}^N \frac{\mu(d)}{d^4} \left[ \sum_{m=1}^{N/d} m^{2-\alpha} \right] \quad (3) \end{aligned}$$

$$\begin{aligned} \text{Now } 1^p + 2^p + \dots + n^p &= \frac{n^{p+1}}{p+1} + o(n^{p+1}) \quad \text{if } p > -1 \\ &= \log n + o(1) \quad \dots \quad \text{if } p = -1 \end{aligned}$$

$$\begin{aligned} \therefore \sum_{m=1}^{\left[ \frac{N}{d} \right]} m^{2-\alpha} &= \log \left[ \frac{N}{d} \right] + o(1) \\ &= \left\{ \log N - \log d + o(1) \right\} \end{aligned}$$

$$\begin{aligned} \therefore \sum_{n=1}^N \frac{\Phi(n)}{n^3} &= \sum_{d=1}^N \frac{\mu(d)}{d^4} \left\{ \log N - \log d + o(1) \right\} \\ &= \log N \sum_{d=1}^N \frac{\mu(d)}{d^4} - \sum_{d=1}^N \frac{\mu(d) \log d}{d^4} + o \left( \sum_{d=1}^N \frac{\mu(d)}{d^4} \right) \\ &= \log N \sum_{d=1}^{\infty} \frac{\mu(d)}{d^4} - \log N \sum_{N+1}^{\infty} \frac{\mu(d)}{d^4} + o(1) \end{aligned}$$

since  $\sum \frac{\mu(d) \log d}{d^4}$  and  $\sum \frac{\mu(d)}{d^4}$  are both convergent

$$\begin{aligned} \therefore \sum_{n=1}^N \frac{\Phi(n)}{n^3} &= \frac{\log N}{\zeta(3)} + o \left( \frac{\log N}{N^2} \right) + o(1) \\ &= \frac{\log N}{\zeta(3)} + o(1) \end{aligned}$$

(c)  $\alpha < 3$ 

We have from (3)

$$\sum_{n=1}^N \frac{\Phi(n)}{n^3} = \sum_{d=1}^N \frac{\mu(d)}{d^4} \sum_{m=1}^{\left[ \frac{N}{d} \right]} m^{2-\alpha}$$

$$\begin{aligned}
 \text{Where } \sum_{m=1}^{\left[\frac{N}{a}\right]} m^{2-a} &= \frac{1}{3-a} \left[\frac{N}{d}\right]^{3-a} + o\left(\frac{N^{3-a}}{d^{3-a}}\right) \\
 &= \frac{1}{3-a} \left(\frac{N}{d}\right)^{3-a} + o\left(\frac{N^{3-a}}{d^{3-a}}\right) \\
 \therefore \sum_{n=1}^N \frac{\Phi(n)}{n^a} &= \sum_{d=1}^N \left\{ \frac{1}{3-a} \frac{N^{3-a}}{d^{3-a}} \frac{\mu(d)}{d^a} \right\} + o\left[ N^{3-a} \sum_{d=1}^N \frac{1}{d^3} \right] \\
 &= \frac{N^{3-a}}{(3-a)} \sum_{d=1}^N \frac{\mu(d)}{d^3} + o(N^{3-a}) \\
 &= \frac{N^{3-a}}{(3-a)} \frac{1}{\zeta(3)} + o(N^{3-a})
 \end{aligned}$$

5. We have  $\Psi(n) + \Phi(n) = n^3$

$$\therefore \sum_{n=1}^N \frac{\Psi(n)}{n^a} + \sum_{n=1}^N \frac{\Phi(n)}{n^a} = \sum_{n=1}^N n^{2-a}$$

$\therefore$  We get from Th. (2)

$$\begin{aligned}
 \sum_{n=1}^N \frac{\Psi(n)}{n^a} &= O(1) \quad \text{if } a > 3 \\
 \sum_{n=1}^N \frac{\Psi(n)}{n^a} &= \log N \left\{ 1 - \frac{1}{\zeta(3)} \right\} + O(1) \quad \text{if } a = 3 \\
 \sum_{n=1}^N \frac{\Psi(n)}{n^a} &= \frac{N^{3-a}}{3-a} \left\{ 1 - \frac{1}{\zeta(3)} \right\} + o(N^{3-a}) \quad \text{if } a < 3.
 \end{aligned}$$

6. We note that for every  $n$   $\Phi(n) > \Psi(n)$

$$\text{For } \frac{\Phi(n)}{n^3} = \left(1 - \frac{1}{p^3}\right) \left(1 - \frac{1}{q^3}\right) \dots \text{ if } n = p^\alpha q^\beta \dots$$

$$\text{And } \frac{\Psi(n)}{n^3} = 1 - \left(1 - \frac{1}{p^3}\right) \left(1 - \frac{1}{q^3}\right) \dots$$

$$\begin{aligned}
 \text{Now } \left(1 - \frac{1}{p^3}\right) \left(1 - \frac{1}{q^3}\right) \dots &> \frac{1}{\zeta(2)} \text{ for every } n \\
 &= \frac{6}{\pi^2} > \frac{1}{2}
 \end{aligned}$$

$$\therefore n^3 \left(1 - \frac{1}{p^3}\right) \left(1 - \frac{1}{q^3}\right) \dots$$

$$> n^{3-n^3} \left(1 - \frac{1}{p^3}\right) \left(1 - \frac{1}{q^3}\right) \dots$$

$$\therefore \Phi(n) > \Psi(n)$$

# \*ON AN ASYMPTOTIC FORMULAE IN THEORY OF NUMBERS

By

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Let  $\pi_2(x)$  denote the number of numbers less than  $x$  and which are products of two different primes. Landau has proved in his "Handbuch Der Lehre von der verteilung der Primzahlen" (Page 208) that

$$\pi_2(x) \sim \frac{x \log \log x}{\log x}$$

I propose to prove that

$$\pi_2(x) = \frac{x \log \log x}{\log x} + \frac{Bx}{\log x} + o\left(\frac{x}{\log x}\right)$$

where B is a constant

$$= \lim_{x \rightarrow \infty} \left\{ \sum_{p \leq x} \frac{1}{p} - \log \log x \right\}$$

Lemma 1.

$$\sum_{p < \sqrt{x}} \pi(p) \sim \frac{2x}{\log^2 x}$$

*Proof*

(a) If  $\sqrt{x}$  is a prime, let  $p_n = \sqrt{x}$  where  $p_n$  denotes  $n^{\text{th}}$

prime

$$\begin{aligned} \text{Then } \sum_{p < \sqrt{x}} \pi(p) &= \pi(2) + \dots + \pi(p_n) \\ &= 1 + 2 + \dots + (n-1) \\ &= \frac{n(n-1)}{2} \end{aligned}$$

$$\text{Now } \pi(\sqrt{x}) = \pi(p_n) = n$$

$$\therefore n \sim \frac{2\sqrt{x}}{\log x}$$

by prime number  
Theorem.

and hence the required result

---

\* I am much indebted to Dr. T. Vijayaraghwan for valuable suggestions in preparing this paper.

(b) Let  $p_n < \sqrt{x} < p_{n+1}$

Then  $\sum_{p < \sqrt{x}} \pi(p) = \pi(2) + \dots + \pi(p_n)$

$$= 1 + 2 + \dots + n = \frac{n(n+1)}{2}$$

And since  $\pi(\sqrt{x}) = \pi(p_n) = n$

$\therefore$  we get the result as before

\*Lemma 2.

$$\sum_{p < \sqrt{x}} \frac{\log p}{p(\log x - \log p)} = \log 2 + o(1)$$

*Proof*

$$\text{Let } F(u, x) = \frac{\log u}{u(\log x - \log u)}$$

Then we have

$$(1) \quad F(u, x) > 0 \quad \text{for } 2 \leq u \leq \sqrt{x}$$

$$(2) \quad \frac{F(u, x)}{\log u} \quad \text{is decreasing in the range } 2 \leq u \leq \sqrt{x}, \text{ and } x \text{ constant.}$$

$$\text{for } \frac{F(u, x)}{\log u} = \frac{1}{u(\log x - \log u)}$$

$$\text{Let } y = y(u) = u(\log x - \log u)$$

$$\text{Then } \frac{dy}{du} = \log x - \log u - 1 > 0$$

$$\text{for } 2 \leq u \leq \sqrt{x}$$

$\therefore y$  is increasing and hence  $\frac{F(u, x)}{\log u}$  is decreasing in range

$$2 \leq u \leq \sqrt{x}$$

$$(3) \quad \frac{F(2, x)}{\log 2} = \frac{1}{2(\log x - \log 2)} = o(1)$$

$$\text{and } I = \int_2^{\sqrt{x}} \frac{du}{u(\log x - \log u)}$$

$$= \int_{\log 2}^{\frac{1}{2} \log x} \frac{ds}{\log x - s}$$

$$= \log \frac{(\log x - \log 2)}{\frac{1}{2} \log x}$$

$$= \log 2 + \log \log x + \log \left( 1 - \frac{\log 2}{\log x} \right) - \log \log x$$

$$= \log 2 + o(1)$$

\* In proving this lemma, we follow closely the method of the theorem on page 203 of Handbuch.

$$\therefore \frac{F(2, x)}{\log 2} = o(1) = o\left\{\int_2^{\sqrt{x}} \frac{du}{u(\log x - \log u)}\right\} = o(1)$$

$$\text{Now } I(x) = \sum_{p \leq x} \log p = x + s(x)$$

$$\text{Where } s(x) = o(1)$$

$$\begin{aligned} \sum_{p \leq \sqrt{x}} \frac{\log p}{p(\log x - \log p)} &= \sum_2^{\lfloor \sqrt{x} \rfloor} \frac{I(n) - I(n-1)}{n(\log x - \log n)} \\ &= \sum_2^{\lfloor \sqrt{x} \rfloor} \frac{1}{n(\log x - \log n)} + \sum_2^{\lfloor \sqrt{x} \rfloor} \frac{n s(n) - (n-1) s(n-1)}{n(\log x - \log n)} \\ &= \sum_2^{\lfloor \sqrt{x} \rfloor} \frac{1}{n(\log x - \log n)} + \sum_2^{\lfloor \sqrt{x} \rfloor} \frac{1}{n s(n)} \left\{ \frac{1}{n(\log x - \log n)} \right. \\ &\quad \left. - \frac{1}{(n+1)(\log x - \log(n+1))} \right\} \\ &+ \frac{1}{2(\log x - \log 2)} + \lfloor \sqrt{x} \rfloor s(\lfloor \sqrt{x} \rfloor) \frac{1}{\lfloor \sqrt{x} \rfloor (\log x - \log \lfloor \sqrt{x} \rfloor)} \end{aligned}$$

Now by (1), (2) and (3)

$$\begin{aligned} &\sum_2^{\lfloor \sqrt{x} \rfloor} \frac{1}{n(\log x - \log n)} + \frac{1}{2(\log x - \log 2)} \\ &= \int_2^{\sqrt{x}} \frac{du}{u(\log x - \log u)} + o\left\{\int_2^{\sqrt{x}} \frac{du}{u(\log x - \log u)}\right\} \\ &= \log 2 + o(1) \end{aligned}$$

Further for all  $u > w = w(\delta)$

$$|s(u)| < \delta$$

$\therefore$  For all  $x > w + 1$

$$\begin{aligned} &\left| \sum_{n=2}^{\lfloor \sqrt{x} \rfloor - 1} \frac{1}{n s(n)} \left\{ \frac{1}{n(\log x - \log n)} - \frac{1}{(n+1)(\log x - \log(n+1))} \right\} \right. \\ &\quad \left. + s(\lfloor \sqrt{x} \rfloor) \frac{1}{(\log x - \log \lfloor \sqrt{x} \rfloor)} \right| \\ &< o(1) + \delta \sum_{n=w}^{\lfloor \sqrt{x} \rfloor - 1} \frac{1}{n} \left\{ \frac{1}{n(\log x - \log n)} - \frac{1}{(n+1)(\log x - \log(n+1))} \right\} \\ &= \delta \sum_{n=w}^{\lfloor \sqrt{x} \rfloor} \frac{1}{n(\log x - \log n)} + o(1) \end{aligned}$$



$$= \delta \int_2^{\sqrt{x}} \frac{du}{u (\log x - \log u)} + o(1) = \delta \log 2 + o(1) = o(1)$$

since  $\delta$  can be taken to be arbitrarily small.

$$\therefore \sum_{p < \sqrt{x}} \frac{\log p}{p (\log x - \log p)} = \log 2 + o(1)$$

We have

$$\pi_2(x) = \sum_{p < \sqrt{x}} f(p)$$

where  $f(p)$  denotes the number of numbers less than  $x$ , and which are products of two different primes, the less of which is equal to  $p$ .

$$\text{Since } f(p) = \pi\left(\frac{x}{p}\right) - \pi(p)$$

$$\therefore \pi_2(x) = \sum_{p < \sqrt{x}} \pi\left(\frac{x}{p}\right) - \sum_{p < \sqrt{x}} \pi(p) \quad \text{--- (1)}$$

Now by Prime number Theorem.

$$\sum_{p < \sqrt{x}} \pi\left(\frac{x}{p}\right) = \sum_{p < \sqrt{x}} \frac{x}{p (\log x - \log p)} + O\left\{ \sum_{p < \sqrt{x}} \frac{x}{p (\log x - \log p)^2} \right\}$$

$$\text{Now } \sum_{p < \sqrt{x}} = \Sigma_1 \quad \therefore \log p < \frac{1}{2} \log x$$

$$\therefore \frac{1}{\log x - \log p} < \frac{2}{\log x}$$

$$\therefore \Sigma_2 = O\left\{ x \sum_{p < \sqrt{x}} \frac{1}{p (\log x)^2} \right\} = O\left\{ \frac{x}{(\log x)^2} \log \log x \right\} \quad \text{--- (2)}$$

$$\Sigma_1 = x \sum_{p < \sqrt{x}} \frac{1}{p (\log x - \log p)}$$

$$= \frac{x}{\log x} \left[ \sum_{p < \sqrt{x}} \frac{1}{p} + \sum_{p < \sqrt{x}} \frac{\log p}{p (\log x - \log p)} \right]$$

$$= \frac{x}{\log x} \left\{ \log \log (\sqrt{x}) + B + o(1) \right\} + \frac{x}{\log x} \left\{ \log 2 + o(1) \right\} \quad \text{by Lemma 2}$$

$$= \frac{x}{\log x} \left\{ -\log 2 + \log \log x + B + \log 2 + o(1) \right\}$$

$$= \frac{x}{\log x} \left\{ \log \log x + B + o(1) \right\} \quad \dots \dots \dots (3)$$

∴ By (1) (2) and (3) and by Lemma (1)

$$\begin{aligned}\pi_1(x) &= \frac{x}{\log x} \left| \log \log x + B + o(1) + o(1) + o(1) \right| \\ &= \frac{x \log \log x}{\log x} + \frac{Bx}{\log x} + o\left(\frac{x}{\log x}\right)\end{aligned}$$

# AN EXPERIMENTAL INVESTIGATION OF DILUTE LIQUID AMALGAMS OF THE ALKALINE EARTHS WITH SPECIAL REFERENCE TO THEIR ELECTRICAL CONDUCTIVITY, VISCOSITY AND DENSITY

By

G. R. PARANJPE and V. S. PATANKAR

## INTRODUCTION

Recently a number of workers have studied the effect of concentration on the physical properties of dilute liquid amalgams of the alkali metals, and their endeavours have thrown some light on the constitution of these amalgams. Thus Bhatnagar, Prasad and Mukerjee<sup>1</sup> have investigated the surface-tension of liquid amalgams of Sodium and Potassium at the amalgam-benzene interface. Bhavs<sup>2</sup> has studied the viscosities of the same amalgams. While Hine,<sup>3</sup> Bohariwalla, Paranjpe and Prasad,<sup>4</sup> and Evans Davies<sup>5</sup> have studied the electrical conductivities.

Unlike some other amalgams, the liquid amalgams of the Alkali metals do not follow the mixture law. The physical property-concentration curves of liquid amalgams of the alkali metals, however, show marked discontinuities at definite concentrations.

These discontinuities have been attributed by some to the formation of compounds or complexes, while others supporting the colloid hypothesis explain them as due to the sudden appearances of new phases. Bent<sup>6</sup> in a recent publication has however shown that the evidence in support of the colloid hypothesis is not conclusive.

Information regarding the liquid amalgams of the Alkaline earths is almost totally lacking. Only a few workers like K. Bornemann and G. V. Raushenplat<sup>7</sup> have determined some of the physical properties, but they confined themselves to one or two concentrations only.

It was, therefore, considered desirable to examine the effect of concentrations on the physical properties, such as electrical conductivities, viscosities and densities of these amalgams.

Before, however, such an investigation could be undertaken, it was necessary to determine the effect of time on the physical properties of these amalgams. For in a recent note by Paranjpe<sup>8</sup> it is pointed out that the viscosity of liquid sodium amalgams decreases

with time and that a mere mechanical agitation is sufficient to restore the initial value.

The results given later on show that no such changes take place in the electrical conductivity and viscosity of the amalgams of the alkaline earths, and it is possible, therefore, to investigate the effect of concentration on the physical properties. To observe the various stages that amalgams undergo on change of concentration, the composition of the amalgams have been varied by very small amounts of the amalgamated metal.

Next, an attempt has been made to verify the theory of electrical conductivity of liquid amalgams put forward by Skaupy.<sup>18</sup> From our experimental results, as well as those of two other workers from this laboratory—Bhave<sup>3</sup> and Bohariwalla<sup>4</sup>—are calculated certain quantities which are of importance in the theory of Skaupy.

Lastly it is shown how the view, taken by Lewis<sup>9</sup> regarding the constitution of amalgams, helps to explain satisfactorily, the behaviour of the liquid amalgams of the alkali metals and alkaline earths.

### EXPERIMENTAL

The general experimental arrangement consists of the following:—

- (i) The preparation of dilute liquid amalgams of the alkaline earth metals of the requisite concentrations.
- (ii) Determination of the concentrations every time before and after the measurement of the physical property under examination.
- (iii) Measurements of the different physical properties, viz.  
(a) electrical conductivity, (b) viscosity and (c) density.

The difficult nature of the problem is evident from the fact, that the alkaline earth amalgams are even more unstable under ordinary conditions than the alkali metal amalgams, and get oxidised very rapidly in air, especially when the latter is moist. All the operations had therefore to be carried out under an atmosphere of an inert gas like nitrogen.

#### I.—*Preparation of the amalgams.*

For the preparation of the amalgams the electrolytic method of T. W. Richards<sup>10</sup> was employed.

As the carbonates of the alkaline earths are very insoluble, saturated solutions of chlorides were employed as the electrolytes. Extra pure Merck's chemicals were used throughout.

Each time the same amount of mercury and the electrolyte was taken. The current strength was maintained at two amperes in all preparations. The different concentrations were obtained by varying only the time of electrolysis.

The amalgams thus prepared were cleaned, dried, and stored in an atmosphere of pure, dry nitrogen (Cf. Bhatnagar and others<sup>1</sup>).

Thus Barium amalgams with concentrations varying from 0.04 to 0.36 grams of Barium per 100 grams of amalgams were prepared. After attaining a concentration of about 0.36 grams % of Barium, the amalgam showed signs of solidifying and hence no higher concentrations were attempted. In the case of strontium amalgams the concentrations were varied from 0.05 to 0.44 grams % of Strontium. In the case of Calcium amalgams it was not possible to attain concentrations higher than 0.023 grams % of Calcium, for after a certain time of electrolysis, increase in the time of electrolysis was not effective in increasing the concentration. The amalgam seemed to decompose as fast as it was formed.

For every experiment a fresh amalgam was prepared.

## II. *Estimation of the concentration :*

(Estimation was done by titration.) A detailed account of the method of estimation is given by Bhatnagar and others.<sup>1</sup>

(Phenolphthaleine used as an indicator gave an end point within 0.1 C.C. of hydroxide. Thus using a 15 gram sample of amalgam, the probable error varied from 1.0 per cent for very dilute amalgams to 0.2 per cent for amalgams of higher concentrations. Every time duplicate analyses of the amalgams were made and the difference between them was never more than 0.5 per cent.)

## III. *The apparatus and the method of measurement :—*

(a) *The electrical conductivity*—The electrical conductivity of amalgams has been measured by Bornemann and Muller,<sup>11</sup> Hine,<sup>3</sup> Williams,<sup>12</sup> T. I. Edwards,<sup>13</sup> A. L. Johns and E. J. Evans,<sup>14</sup> and Bohariwalla and others,<sup>4</sup> by the potentiometer method.

The same method for measuring the conductivities has been used in this investigation and a full description of it is given by Bohariwalla and others.<sup>4</sup>

The value of the standard resistance was 0.3410 ohm, and as the current strength chosen was about 29 milliamperes the potential difference across it was about  $1 \times 10^{-3}$  volts. The galvanometer was sensitive enough to give a deflection when the balance was upset by  $3.0 \times 10^{-6}$  volts.

$$\text{Now } R_m = \frac{R_k}{L_k} \times L_m.$$

where  $R_m$  = Resistance of cell containing the amalgam.

$R_k$  = Resistance of the standard.

$L_m$  = Fall of potential across the cell.

and  $L_k$  = Fall of potential across the standard.

$$\begin{aligned}\text{therefore } d(R_m) &= \frac{Rk}{Lk} \times d(L_m) \\ &= \frac{0.3410}{1.0 \times 10^{-3}} \times 3.0 \times 10^{-4} \\ &= 0.0001 \text{ ohms approximately.}\end{aligned}$$

Thus a change of resistance of 0.0001 ohm could be detected with this arrangement. (The actual error was much less than this as the mean of about ten observations with different current strengths was taken each time)

(b) *Viscosity*:—The measurement of the coefficients of viscosity of these amalgams was first attempted by the Thorpe and Rodgers type viscometer. This type of viscometer was used by Bhavs<sup>3</sup> for the measurement of viscosities of Sodium and Potassium amalgams. But the alkaline earth amalgams were found to stick to glass and thus the measurement of levels by means of a cathetometer became impossible. Moreover it was required to investigate the effect of time on the viscosities of the amalgams without disturbing them in any way, and this was not possible with the above-mentioned arrangement. It was therefore finally given up and an altogether new apparatus was designed.

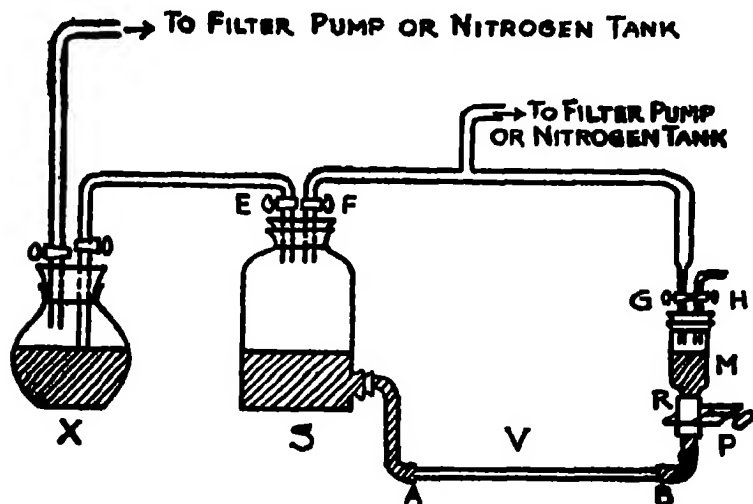


Fig 1.

The new apparatus as shown in fig. 1 consists of three parts. S is a bottle used as a storing vessel. V is the viscometer attached to S by means of a rubber cork covered with a layer of paraffin wax. The viscometer consists of a capillary tube AB, to the two ends of which were attached two broad glass tubes bent in the form as shown in fig. (1). The capillary, which was carefully calibrated and found to

be uniform, had a length of about 28 cms. and a bore of radius 0.03073 cm. M the small cylindrical measuring vessel of uniform bore was attached to the viscometer by means of a small piece of pressure tubing. Both the storing and the measuring vessels were closed by air-tight rubber corks. Through these corks passed glass tubes with stop-cocks and thus both these vessels could be connected either to the filter pump or to the tank of nitrogen. The measuring vessel M could be closed from the rest of the apparatus by means of a pinch cock P

Before each experiment the different parts of the apparatus were disconnected, thoroughly cleaned and joined again as shown in fig (1). To make the apparatus air tight all the joints were covered on the outside with a layer of resin-wax mixture.

The vessel X containing the freshly prepared amalgam was then connected to the storing vessel S by means of two short pieces of pressure tubing and a glass tube as shown in fig. (1). The glass stop-cock E was then closed and the further end of the viscometer V was closed by means of the pinch-cock P. Then F was opened and the vessel S and the viscometer V were evacuated as completely as possible. They were then filled with pure, dry nitrogen, and again evacuated. The stop-cock E was then opened, and after drawing by suction a sufficient quantity of the amalgam from X in S, the stop-cock E was again closed. The vessel X was then detached and S was filled with pure, dry nitrogen.

The whole apparatus was contained in an electrically operated air-thermostat. The temperature of the thermostat was maintained at a steady value of 30°C. The vessel M was adjusted in a vertical position and a slow steady stream of nitrogen was sent through the vessels S and M by opening F and G to the nitrogen tank and E and H to the atmosphere. As the stop-cocks E and H were opened to the atmosphere, both the vessels were at atmospheric pressure throughout the following procedure.

After adjusting the cathetometer, the pinch-cock P was released and the amalgam allowed to flow into M. The levels of the rising meniscus of the amalgam in M were noted down by the cathetometer against time, until a final steady level was reached. The level in S at any previous instant was calculated from the value of this steady level and the amount of amalgam that had flowed into M since then.

Knowing the levels of the meniscus in M at any two instants, the quantity of the amalgam that had flowed through the capillary of the viscometer during that interval could be calculated from the known cross-section of M. The pressure-head on the viscometer could be calculated from the levels in M and S. Thus all the quantities

necessary for the calculation of the coefficient of viscosity, from the equation,

$$\eta = \frac{\pi}{8} \frac{g \rho h \alpha^4}{Q} t.$$

for the flow through a capillary, were known, except  $\rho$ , the density, which was determined each time by a separate experiment. The coefficient of viscosity could thus be calculated.

No kinetic energy correction need be applied, as only relative values of the coefficients of viscosity are required.

The final steady level which the amalgam would attain was approximately known before-hand. The cathetometer was adjusted about a centimeter below this and as soon as the meniscus passed this level a stop-watch was started. The cathetometer was then adjusted one or two millimeters higher, and the time noted in the stop-watch when the meniscus passed the cross-wire. This procedure was followed until the steady state was attained. The measurements of heights and times were thus made in succession, and an error committed either in the measurement of level or time in one observation, resulted in an equal and opposite error in the next observation. Thus in the calculation of the coefficient of viscosity the error from one observation was partly eliminated by about an equal and opposite error in the next. Thus the mean of about six or seven consecutive observations yields quite a reliable value.

The error in an individual observation was from 2 to 3 per cent; but since each experiment consisted of about six or seven consecutive observations and, as explained above, the error in one observation was partly neutralised by about an equal and opposite error in the next, the probable error in the mean was never more than 0.5 per cent. This is quite evident from the following values of the coefficients of viscosity of mercury obtained with the apparatus at three different times:—

Temperature.	$\eta$ obtained by the author.	$\eta$ calculated from S. Koch's formula	% error.
31.0°C.	0.01514	0.01511	0.20
31.0°C.	0.01513	0.01511	0.13
32.0°C.	0.01512	0.01506	0.39

(c) *Density* —The densities of the amalgams were determined under liquid paraffin by means of a specific gravity bottle.

The amalgam was never exposed to the air except during the act of transferring it to the specific gravity bottle. The determinations of



the coefficients of viscosity and density were made at the same temperature.

### RESULTS

#### (i) *Effect of time on the physical properties of amalgams of the alkaline earth metals*

A large amount of amalgam was prepared and stored under an atmosphere of pure, dry nitrogen, so that it kept its strength unaltered during the course of the experiment. The physical property, *i.e.* either the electrical conductivity or the viscosity was determined from day to day as described in the experimental part

The results of the experiments are given in Tables I and II.

#### *Effect of time on the amalgams.*

TABLE I.—Electrical Conductivity.

Time.	BARIUM		STRONTIUM	
	Concentration	Resistivity. $\times 10^{-6}$	Concentration.	Resistivity. $10^{-6}$
First day	0.1337	96.81	0.0552	96.54
Second day	0.1331	96.83	0.0550	96.56
Third day	0.1325	96.79	...	...
First day	0.2853	96.91	0.1714	96.10
Second day	0.2850	96.92	0.1733	96.12
First day	...	..	0.4545	94.80
Second day	...	...	0.4662	94.80

#### *Effect of time on the amalgams.*

TABLE II.—Viscosity

Time	BARIUM		STRONTIUM	
	Concentration	Viscosity.	Concentration.	Viscosity.
First day	0.2026	0.01737	0.0751	0.01644
Second day	0.2010	0.01741	0.0735	0.01630
Third day	0.2008	0.01751	..	...
First day	0.2389	0.01748	0.1057	0.01678
Second day	0.2346	0.01748	0.1045	0.01678
First day	0.1789	0.01681	...	...
Second day	0.1785	0.01700	...	...
First day	0.1525	0.01692	...	...
Second day	0.1519	0.1698	..	...

Viscosity determinations in the case of Barium amalgams were made at 32°C ; while those of the Strontium amalgams were made at 30°C.

The results show that, in the case of these amalgams, no changes take place, with time, in the electrical conductivity and viscosity. The slight changes, that are observed, are within the limits of experimental errors. It was, therefore, concluded that the amalgams of Barium and strontium metals are fairly homogeneous and stable.

Incidentally these experiments prove that the amalgams keep up their concentrations, when stored under the conditions employed. They also furnish evidence for the reproducibility of the results

(ii) *Variation of the electrical conductivity with concentration*

The results of the determinations of electrical conductivities at different concentrations of Barium, Strontium and calcium amalgams are given in table III, IV and V respectively. In each case the concentration has been expressed in two ways, once in terms of the number of gms of the metal in 100 gms of the amalgam, and second time in number of gm-atoms of the metal in 100 gm atoms of mercury.

TABLE III

*Electrical conductivities of Barium amalgams at 30°C.*

Resistivity of mercury at 30°C. =  $96.69 \times 10^{-6}$

Conductivity " " " " =  $1.0342 \times 10^4$

Concentration		Resistivity of amalgam $\times 10^{-6}$	Conductivity of amalgam $\times 10^4$
in gms. % of Ba.	in gm atoms % of Ba.		
0.0412	0.0602	96.77	1.0333
0.1285	0.1878	96.96	1.0313
0.1337	0.1954	96.81	1.0329
0.1805	0.2640	96.87	1.0323
0.2040	0.2983	96.90	1.0320
0.2249	0.3291	96.83	1.0327
0.2338	0.3422	96.83	1.0327
0.2658	0.3890	96.88	1.0323
0.2853	0.4178	96.91	1.0319
0.3200	0.4687	96.96	1.0313
0.3327	0.4874	96.80	1.0330
0.3351	0.4906	96.79	1.0331
0.3572	0.5234	96.85	1.0325

TABLE IV

*Electrical conductivities of Strontium amalgams at 30°C.*Resistivity of mercury at 30°C. =  $96.69 \times 10^{-8}$ Conductivity " " " " =  $1.0342 \times 10^4$ 

Concentration		Resistivity of amalgam $\times 10^{-8}$	Conductivity of amalgam $\times 10^4$
in gms % of Sr.	in gm-atoms. % of Sr		
0.0552	0.1264	96.54	1.0356
0.1297	0.2974	96.27	1.0386
0.1714	0.2877	96.10	1.0406
0.2201	0.5051	95.94	1.0423
0.2890	0.6636	95.66	1.0453
0.3877	0.8910	95.30	1.0492
0.4275	0.9833	95.01	1.0526
0.4545	1.0460	94.80	1.0547

TABLE V

*Electrical conductivities of Calcium amalgams at 30°C*Resistivity of mercury at 30°C. =  $96.69 \times 10^{-8}$ Conductivity " " " " =  $1.0342 \times 10^4$ 

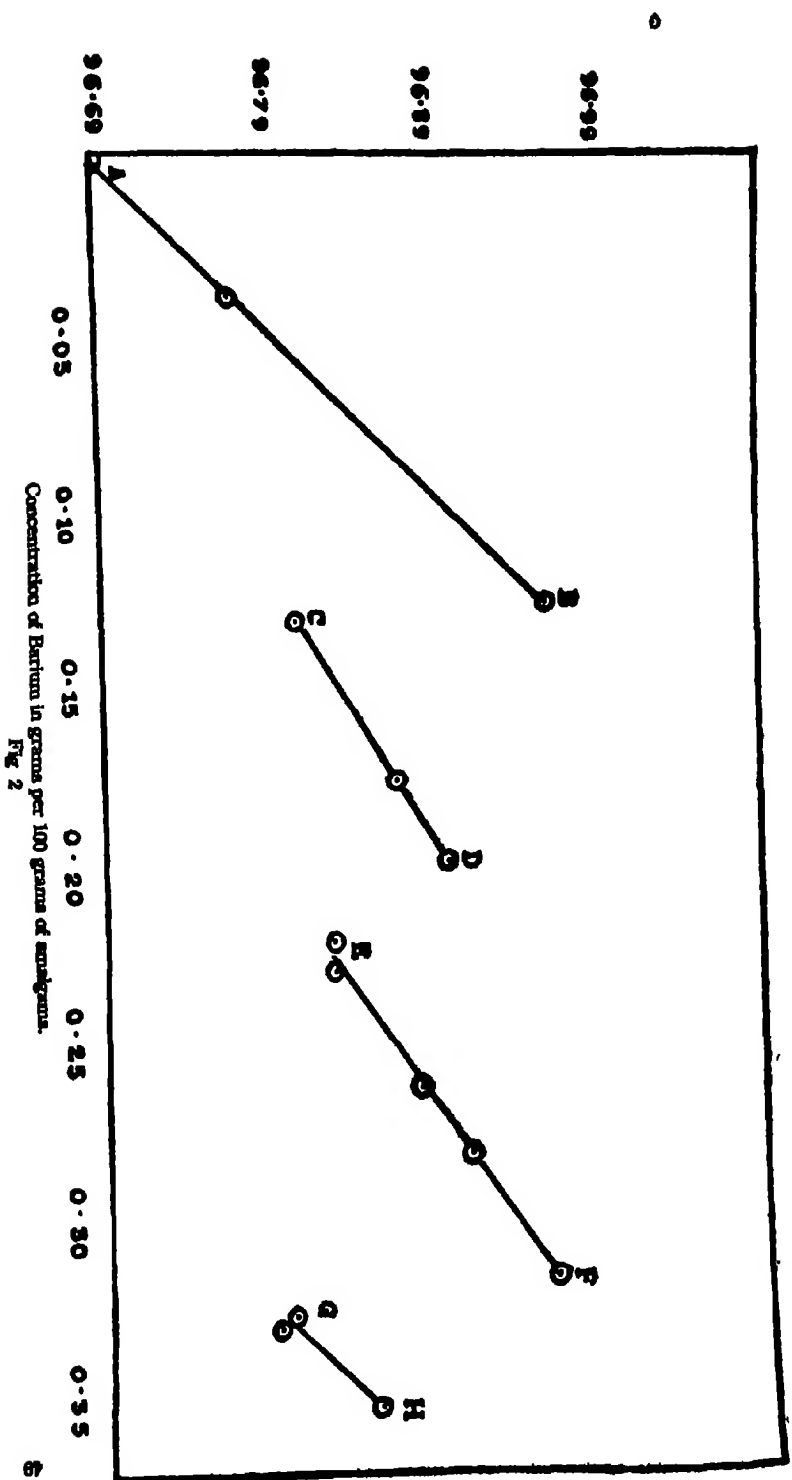
Concentration		Resistivity of amalgam $\times 10^{-8}$	Conductivity of amalgam $\times 10^4$
in gms.% of Ca.	in gm-atoms % of Ca.		
0.0097	0.0485	96.56	1.0356
0.0206	0.1031	96.46	1.0366
0.0225	0.1127	96.40	1.0373
0.0236	0.1181	96.40	1.0373

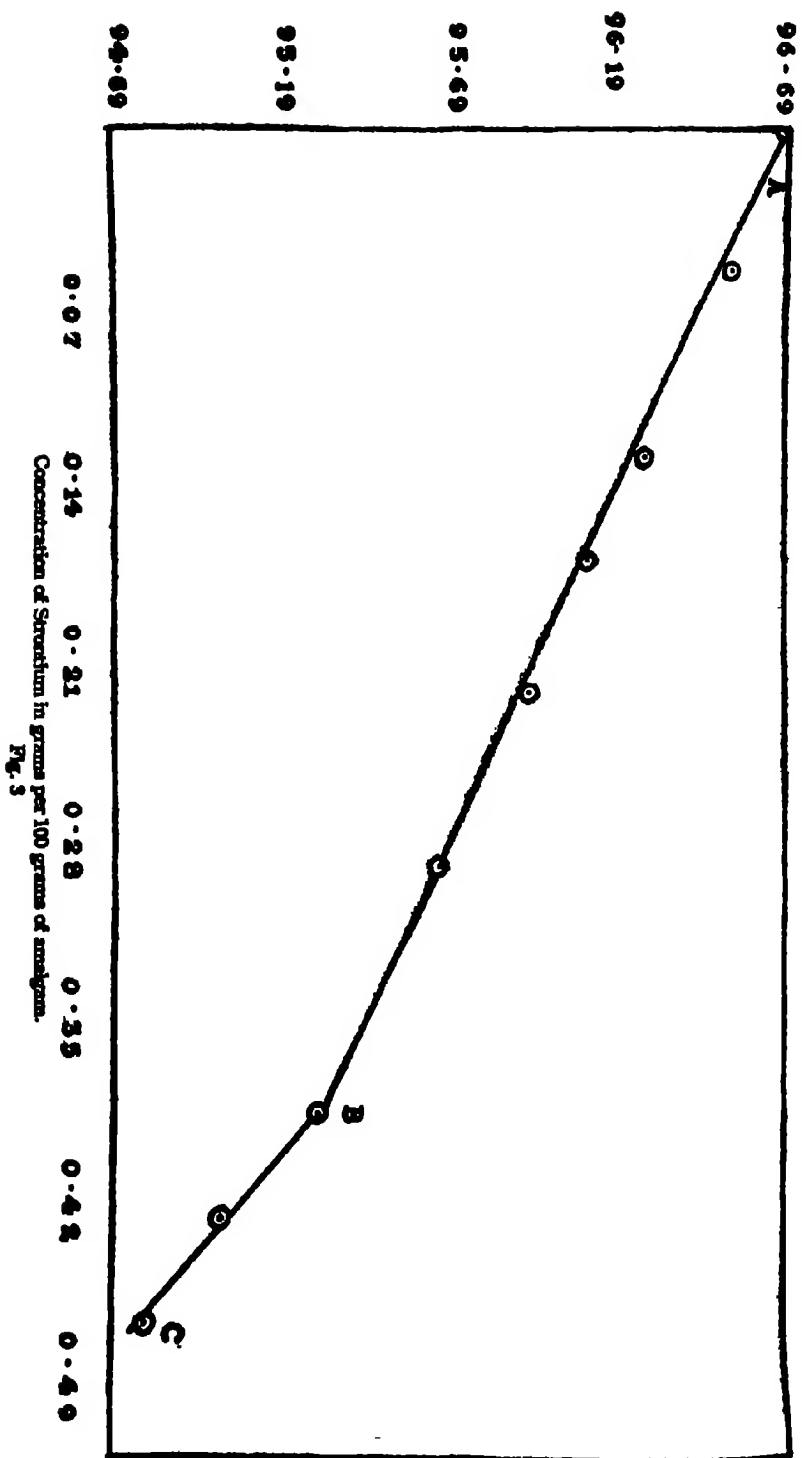
The resistivities of all the three amalgams are plotted down as ordinates against their respective concentrations as abscissa and the curves so obtained are given in figs. (2), (3) and (4).

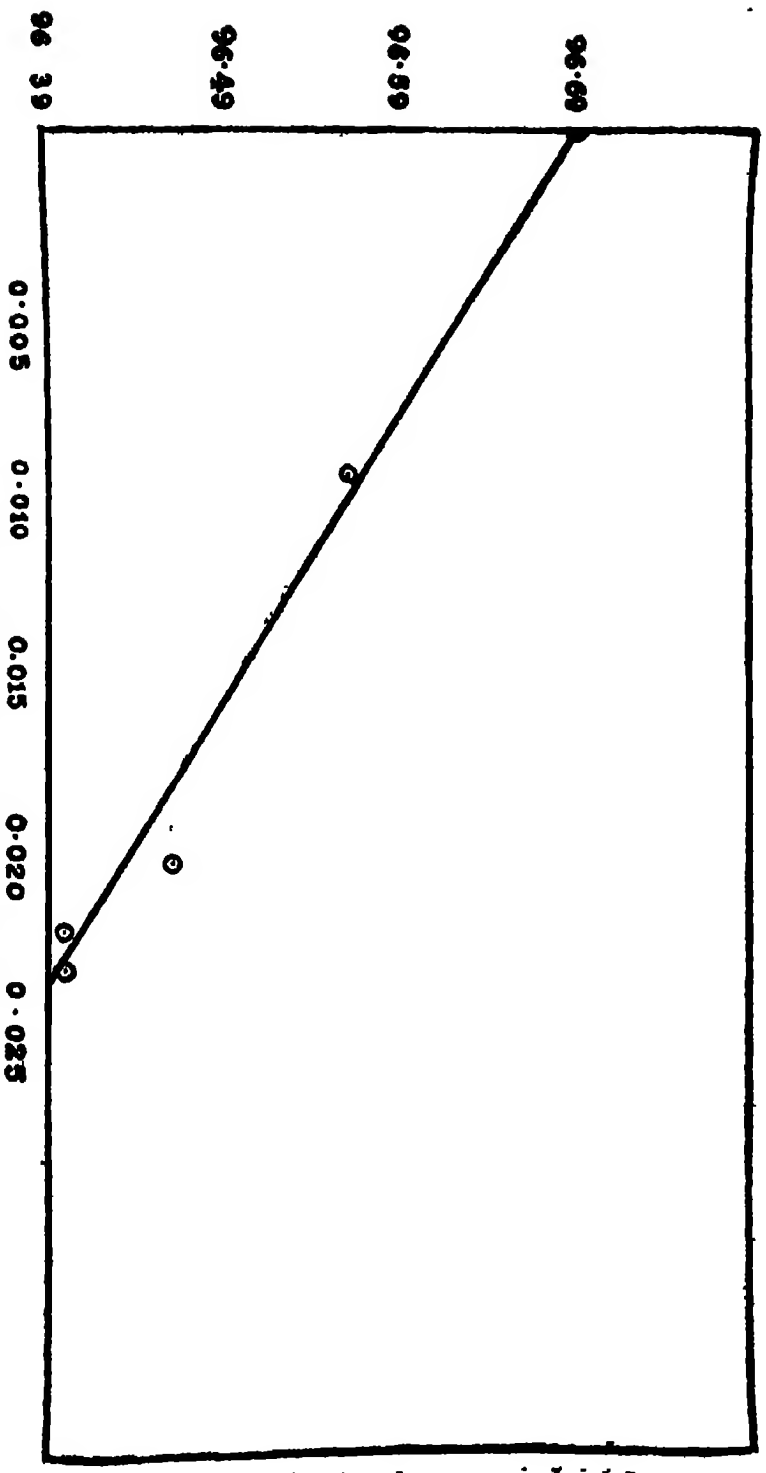
Starting with pure mercury at the point A fig (2) the resistivity of Barium amalgam increases uniformly with concentration until it reaches a maximum at about the point B, corresponding to the concentration 0.130 gms % Barium. After this concentration, there is a sharp break in the curve with an abrupt decrease in the resistivity.

From the point C the resistivity again increases uniformly with concentration till the second discontinuity is reached at the point D, corresponding to the concentration of about 0.225 gms. % Barium.

A third discontinuity occurs at the point F, corresponding to the concentration of about 0.325 gms. % Barium.







Concentration of Calcium in grams per 100 grams of sample.

Fig. 4.

In the case of Strontium the addition of this metal decreases the resistivity of mercury. Thus starting with pure mercury at the point A fig. (3), the resistivity decreases uniformly with concentration till the point B, corresponding to the concentration of about 0.39 gm. % Strontium, is reached. After this concentration the rate of decrease of resistivity with concentration suddenly increases.

The range investigated in the case of Calcium amalgam is small; but in this region of concentrations the amalgam exhibits no peculiarities, and the resistivity decreases uniformly with concentration.

(iii) *Variation of viscosity with concentration* :—

This investigation was confined only to the Barium amalgams; for of the three amalgams under consideration it is only the Barium amalgam that exhibits discontinuities on the conductivity-concentration curve. The results of the investigation are given in table 6.

TABLE VI.

*Viscosities of the Barium amalgams at 32° C.*

Coefficient of Viscosity of mercury at 32° C. = 0.01506

Density " " " " = 13.516 gm/c.c.

Concentration.		Density in gms. per c.c.	Coefficient of viscosity
in gms. % of Ba.	in gm-atoms % of Ba.		
0.0540	0.0789	13.50	0.01593
0.0844	0.1233	13.50	0.01656
0.1238	0.1810	13.49	0.01736
0.1522	0.2225	13.48	0.01695
0.1787	0.2613	13.47	0.01690
0.2026	0.2964	13.47	0.01737
0.2367	0.3463	13.47	0.01748
0.2671	0.3910	13.46	0.01708
0.3018	0.4419	13.46	0.01776
0.3124	0.4576	13.45	0.01794
0.3443	0.5044	13.44	0.01773
0.3641	0.5334	13.44	0.01731

As can be gathered from table 6, the general effect of adding Barium even in small quantities to mercury is to increase the viscosity considerably. The coefficients of viscosity of twelve different Barium amalgams, containing from 0.0540 gms. % to 0.3641 gms. % of Barium have been determined.

The viscosity coefficients of the Barium amalgams have been plotted as ordinates against the respective concentrations as abscissae, and the curve so obtained is given in fig. 5

The results definitely indicate the existence of three maxima in the curve, in the range investigated, and that these maxima are situated at about the concentrations 0.125, 0.220 and 0.323 gms. % of Barium, i.e., at almost the same concentrations at which the discontinuities occur in the electrical conductivity concentration curve (fig. 2)

(iv.) *Variation of Density with concentrations*.—The determinations of the densities were also confined only to the Barium amalgams. The results are given in column three, table VI.

The density uniformly decreases with increase in concentration, and the density concentration curve exhibits no peculiarities. (Fig. 6) If such actually exist, they are not prominent enough to be detected by method of measurement employed here.

(v) *Verification of Skaup's theory*.—Skaup<sup>18</sup> bases his theory on an analogy between liquid metals and electrolytic solutions, and assumes that the electrical conductivity of a pure solvent must be expressed as a function of the concentration of electrons and of the internal friction  $l$ ,  $e$ , viscosity.

He further assumes that dilute metallic solutions must show a higher electron concentration than the solvent as splitting off of the electrons occurs when the dissolved substance dissociates. The splitting up of neutral molecules into ions and electrons is in accord with the law of mass action.

The conductivity  $L$  of a metallic liquid is proportional to the electron concentration  $e$ , and inversely proportional to the internal friction (viscosity)  $\eta$ , and can be written

$$e = \text{constant} \times L \times \eta \quad \dots \dots \dots (1)$$

Taking logarithms of both sides and differentiating we obtain

$$\frac{1}{e} \Delta e = \frac{1}{L} \Delta L + \frac{1}{\eta} \Delta \eta \quad \dots \dots \dots (2)$$

Let  $C$  = concentration of the substance dissolved in mercury expressed in gm. atoms per hundred gm. atoms of mercury. Dividing by  $C$  the equation (2) becomes

$$\frac{1}{e} \frac{\Delta e}{C} = \frac{1}{L} \frac{\Delta L}{C} + \frac{1}{\eta} \frac{\Delta \eta}{C} \quad \dots \dots \dots (3)$$

$\Delta$  expresses that we are dealing with finite changes however small corresponding to small but finite concentrations, and we can substitute for  $L$  and  $\eta$  the values for the pure solvent.

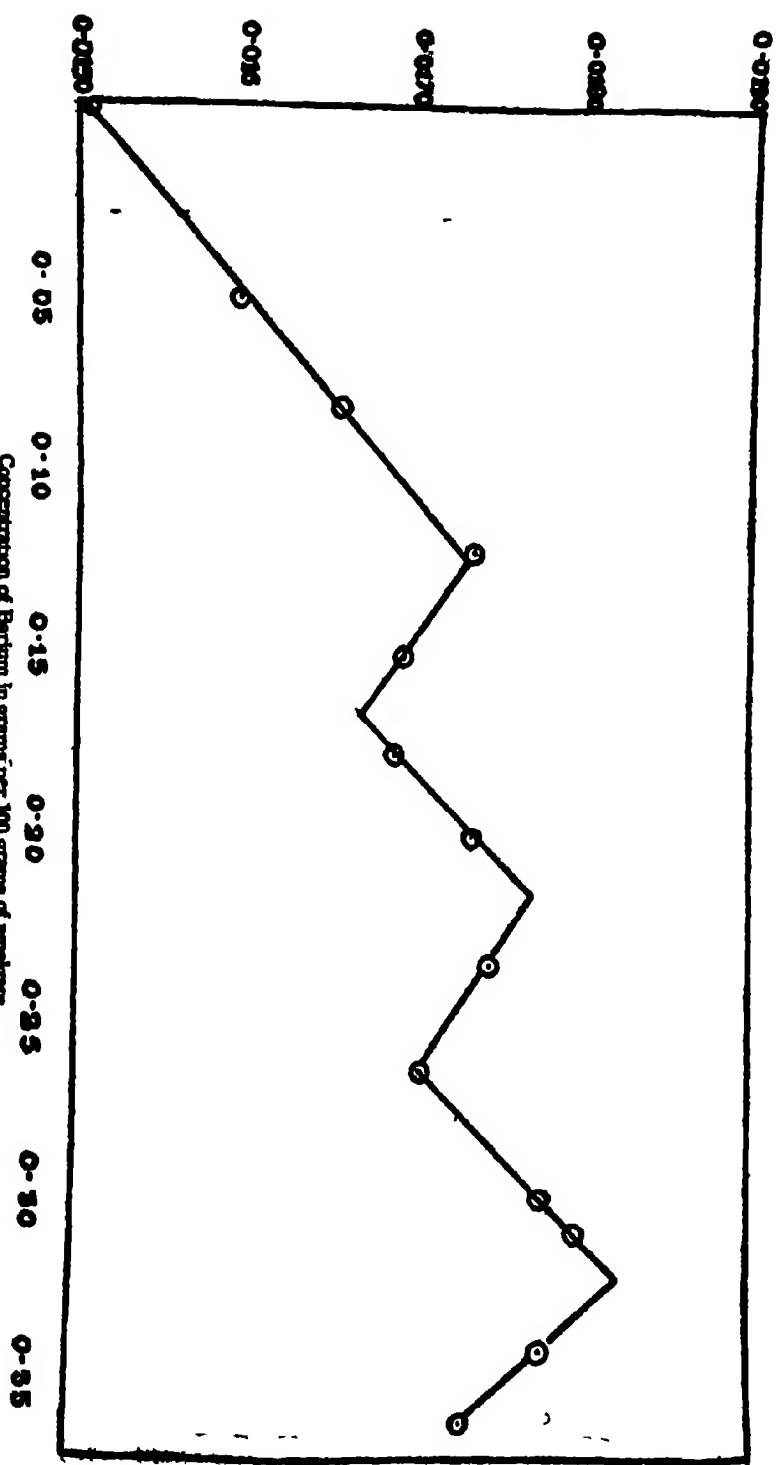
Putting

$$\frac{1}{e} \frac{\Delta e}{C} = H, \quad \frac{1}{L} \frac{\Delta L}{C} = l \quad \text{and} \quad \frac{1}{\eta} \frac{\Delta \eta}{C} = r$$

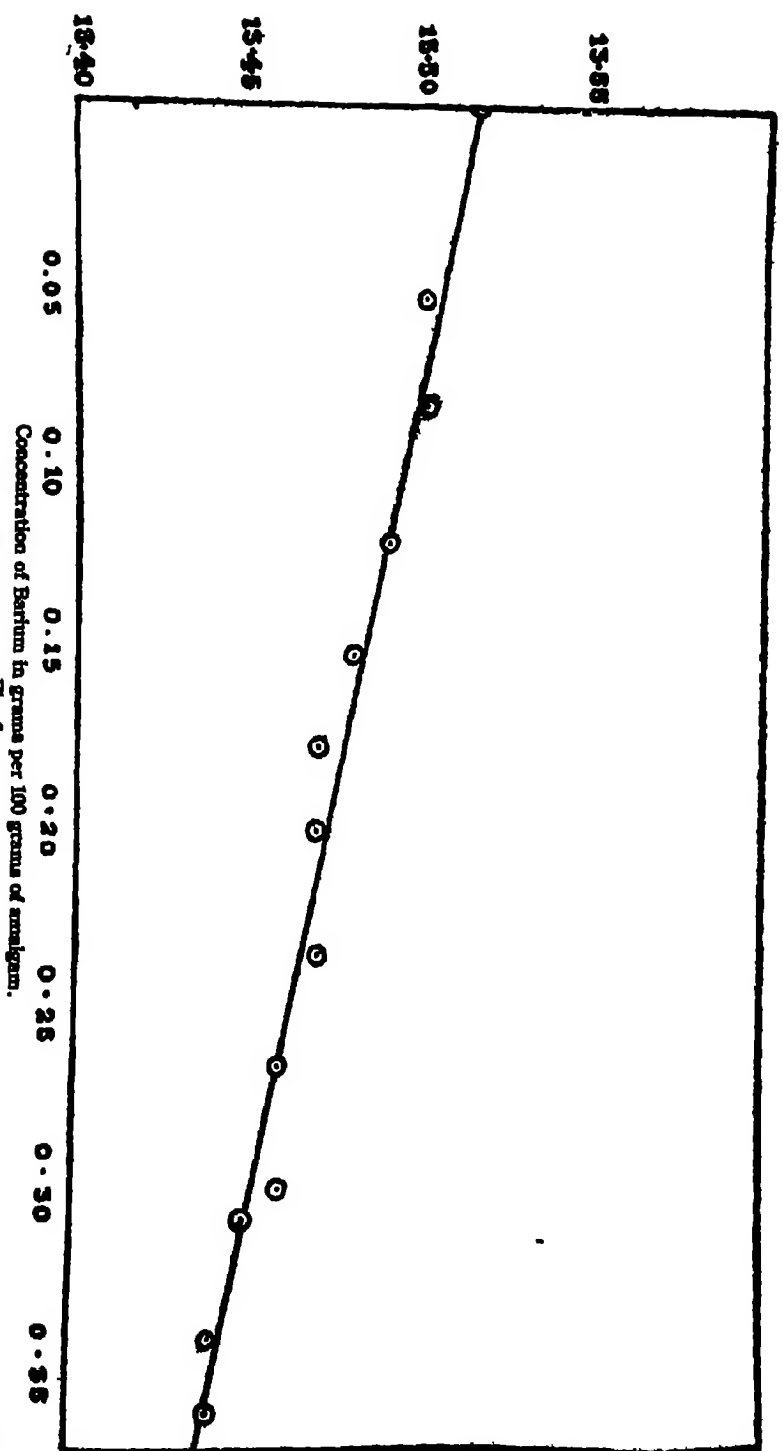
we obtain from (3)

$$H = l + r$$





Concentration of Barium in grams per 100 grams of sample.



Concentration of Barium in grams per 100 grams of amalgam.  
Fig. 6.

which for infinite dilution can be expressed as

$$H_a = l_a + r_a$$

Skaupy showed in the first paper that  $l_a$  has approximately the same value for a number of metals dissolved in mercury.

The rule that  $l_a$  has approximately the same value for all metals does not hold in the case of some alkali amalgams, for  $l$  has a negative value in these cases. The difficulty was not removed until H. Fenniger's work<sup>16</sup> showed the increased value of the viscosity for these amalgams.

If this is taken into account, we obtain the more general rule that

$$H_a = l_a + r_a$$

should have the same order of magnitude for different metals dissolved in mercury.

The necessary quantities are calculated and are entered in table 7.

TABLE VII.

Co-efficient of viscosity of mercury at 30°C. = 0.01516.

Electrical conductivity " " " =  $1.0342 \times 10^6$ .

	Concentration. (C)	Conductivity $\times 10^4$ (L)	Viscosity co-efficient ( $\eta$ )	$\frac{\Delta L}{L} \frac{1}{c} = l$	$\frac{\Delta \eta}{\eta} \frac{1}{c} = r$	$H = l + r$
Ba. Amalgam	0.1810	1.0317	0.01736	-0.0134	0.8437	0.8303
	0.2964	1.0320	0.01737	-0.0072	0.5175	0.5103
	0.4419	1.0316	0.01776	-0.0056	0.4049	0.3992
	0.5044	1.0328	0.01773	-0.0027	0.3516	0.3489
Sr. Amalgam	0.1264	10.356	0.01598	0.0092	0.4224	0.4316
	0.2974	1.0386	0.01708	0.01269	0.4233	0.4360
Na. Amalgam	0.4571	1.0178	0.0226	-0.07381	1.081	1.004
	2.604	1.0247	0.01856	-0.0028	0.0833	0.0805
K. Amalgam	0.3482	1.0058	0.01858	-0.07886	0.6045	0.5257
	0.3594	1.0027				
			0.01767	-0.05446	0.2823	0.2279

N.B.—These conductivity and viscosity values of the amalgams are at about 30°C. Values of the electrical conductivities and viscosities for the Sodium and Potassium amalgams have been obtained from the works of Bohariwala<sup>4</sup> and Bhawe.<sup>3</sup>

The values of  $H$  are given in the last column of table 7 for four different amalgams viz., those of Barium, Strontium, Sodium, and Potassium.

The values of  $H$  have a tendency to increase with decreasing concentrations in all except the Strontium amalgam. Thus it appears that

values of  $H\alpha$  for these amalgams will have a much greater value than those at the concentrations given.

The values of  $H\alpha$  for Gold and other amalgams have been shown by Skaupy,<sup>10</sup> Williams,<sup>11</sup> etc., to be of the order of 0.10. Thus values of  $H\alpha$  for these amalgams will differ appreciably from the values expected from the rule that  $H\alpha$  is of the same order of magnitude for all metals dissolved in mercury. It, thus, seems that this rule does not hold good for the four amalgams examined.

### DISCUSSION.

The results of the work done on dilute liquid amalgams of Barium by the authors and other workers bring out the remarkable similarity between this amalgam and those of Sodium and Potassium. Thus Barium, like Sodium and Potassium when dissolved in mercury lowers the conductivity of the latter. The conductivity-concentration curve of Barium amalgam exhibits discontinuities at certain concentrations. The conductivity-concentration curves of Sodium and Potassium also exhibit similar discontinuities (Bohariwala<sup>4</sup>). The viscosity-concentration curve of Barium amalgam shows maxima at the concentrations where the discontinuities exist on the conductivity-concentration curve. The viscosity-concentration curves of Sodium and Potassium amalgams also exhibit similar maxima (Bhave<sup>3</sup>). On the passage of an electric current through dilute liquid amalgams of Sodium, Potassium and Barium, the amalgamated metal gathers round the anode (Lewis, Adam and Lanmann<sup>6</sup>; Le Blanc and Jacks<sup>17</sup>). But the transference of the metals, Sodium, Potassium and Barium, towards the anode holds good upto a certain concentration only (2.0% Na, 2.5% K. and 2.7% Ba); after this concentration a reversal in the direction of migration takes place, in each case towards the cathode (R. Kremann and co-workers<sup>18</sup>). Thus the behaviour of dilute liquid amalgams of Barium is in every respect similar to the behaviour of the dilute liquid amalgams of Sodium and Potassium.

The Strontium and Calcium amalgams, however, resemble the Lithium amalgam. On the addition of Strontium or Calcium the electrical conductivity of mercury increases. Lithium when dissolved in mercury has also been shown to increase the conductivity of the latter (Hine<sup>5</sup> and Bohariwala<sup>4</sup>). On the passage of a current through dilute liquid amalgams of these metals, the amalgamated metal gathers round the cathode in each case (Le Blanc and Jacks<sup>17</sup>; R. Kremann and co-workers<sup>18</sup>).

The dilute liquid amalgams of the alkali and alkaline earth metals can thus be grouped into two classes. The first comprises the Sodium, Potassium and Barium amalgams and the second those of Lithium, Strontium and Calcium.

The outstanding features of the first group are that, the electrical conductivities of amalgams belonging to this group are less than that of pure mercury, and that on the passage of a current through these dilute amalgams, the amalgamated metal travels to the anode.

The features of the second group are that, the electrical conductivities of amalgams in this group are greater than that of pure mercury, and that on the passage of a current through dilute liquid amalgams of this group, the amalgamated metal goes to the cathode.

The behaviour of both these groups can be explained in the following manner.

When a metal is dissolved in a non-metallic solvent, as Sodium in liquid ammonia, it dissociates according to the theory of Kraus,<sup>10</sup> into positive ions ( sodium ions ) and negative electrons, which may be, in part, combined with the molecules of the solvent. When an electric current is passed through such a solution, the dissolved metal is carried with the positive current.

It does not seem unreasonable if we assume, like Lewis, Adams and Lanmann<sup>9</sup> that the alkali and alkaline earth metals, when dissolved in a far less positive metal like mercury, would behave in a like manner.

Thus any of these metals, when dissolved in mercury would get ionised to a considerable extent, the concentration of electrons would increase and there would be an increase in the conductivity of the amalgam. Moreover on the passage of a current through dilute amalgam of any of these metals the positive ion ( the alkali or alkaline earth metal ion in this case ) would travel towards the cathode.

But, as mentioned earlier, experiments prove that the behaviour of dilute solutions of Sodium, Potassium and Barium in mercury is exactly contrary.

Lewis, Adams and Lanmann<sup>9</sup> have explained this peculiar behaviour in the following words.—

" A clue to the interpretation of this apparently mysterious transference effect in amalgams is found when we examine the curves relating the electrical conductivities and the compositions of liquid amalgams of Sodium and Potassium. Bornemann and Muller have shown that the electrical conductivity of mercury is lowered by the addition of Sodium.

Now, unless the Sodium diminishes the number of electrons which take part in the conduction, which seems improbable, this change of conductivity must be due to a diminution of the average mobility of the electrons. Probably the atoms of Sodium which are dissolved in mercury, are not there chiefly as such, but rather as nuclei of large aggregates of mercury atoms. Be this as it may, we can consider a dilute amalgam as composed of small regions whose centres are the

Sodium atoms, embedded in a mass which has all the properties of pure mercury. If an electron meeting one of these regions during the passage of the current is on the average retarded, whether by the greater impenetrability of that region or by any kind of reflection or refraction then, by the law of action and reaction, the region containing the Sodium atom will be impelled in the direction of the negative current."

This explanation of Lewis, Adams and Lanmann<sup>9</sup> at once explains the decrease in conductivity and the transference of the amalgamated metal towards the anode in the case of Sodium, Potassium and Barium amalgams. But this assumption of the process of solvation, or the combination with the solvent, is not only necessary to explain the behaviour of Sodium, Potassium and Barium amalgams. This hypothesis is necessary in the case of Calcium, Strontium and Lithium amalgams. For the amalgams of the alkali and alkaline earth metals behave abnormally as regards their vapour pressure, solution tensions and diffusion velocities (Ramsay<sup>20</sup>; C. McP. Smith<sup>21</sup>). The assumption of solvation satisfactorily explains these abnormalities

C. McP. Smith<sup>21</sup> explained this behaviour on the assumption that compound formation takes place and the molecule of the compounds thus formed contains only one atom of the amalgamated metal and a number of atoms of mercury. Thus his idea of compound formation is not however much different from the solvation process which Lewis, Adams and Lanmann imagine.

It can thus be assumed that an alkali or alkaline earth metal on going into solution in mercury first gets ionised, splitting into electrons and positive ions. The mercury atoms then gather on the positive ions, thus forming an aggregate of mercury with the positive ion as nucleus. The degree of solvation is, however, different for different metals.

The concentration of the electrons is thus increased, but the electrical conductivity which depends also on the mobility of electrons will increase or decrease according as the mobility of the electrons increases or decreases. If the solvation is considerable the mobility of electrons, as explained above, decreases considerably and the conductivity decreases; but if the solvation is not much, the mobility of the electrons is not changed appreciably and the conductivity increases.

The positive ion with its aggregate of mercury atoms has a tendency, due to the imposed E.M.F., to travel towards the cathode; but due to the bombardment of the electrons, on the passage of the electric current, the positive ion with its aggregate of mercury atoms is repelled towards the anode. The direction of transference of the metal depends on which of these two tendencies predominates. If there is good deal of solvation the amalgamated metal is forced towards the anode. If

the solvation is not appreciable the amalgamated metal moves towards the cathode. Thus whether the conductivity will decrease and the metal will travel towards the anode or whether the conductivity will increase and the amalgamated metal will travel towards the cathode is determined by the degree of solvation which the metal undergoes. If the solvation is considerable the conductivity decreases and the metal travels towards the anode. To this class belong the dilute amalgams of Sodium, Potassium and Barium. If the solvation is not considerable, the conductivity increases and the metal travels towards the cathode. This is what happens in the case of dilute amalgams of the Lithium, Strontium and Calcium metals.

The reversal in the direction of migration during electrolysis which R. Kremann<sup>18</sup> and others observed in the case of liquid Sodium, Potassium and Barium amalgams at concentrations 2.0% Sodium, 2.5% Potassium and 2.7% Barium, can be explained as the tendency, of going to the cathode, of the positive ion with its aggregate of mercury atoms, attaining predominance at these concentrations over its repulsion towards the anode due to the bombardment of electrons.

The departure exhibited by the amalgams of Sodium, Potassium, Barium and Strontium from Skaupy's theory of conduction, for the liquid amalgams, becomes clear from this point of view; for Skaupy assumed that the amalgamated metal dissociates into electrons and positive ions on going into solution with mercury and that the positive ions exist as such in the solution. But due to the solvation that takes place, the viscosity increases abnormally, and the value of  $H\alpha$  in these cases has therefore a much higher value than those for other metals.

The assumption of the process of solvation is further supported by the investigations of Bhav<sup>2</sup> on the viscosities of dilute amalgams of Sodium, and Potassium, and those of the authors on Barium amalgams, record in this paper. The viscosity-concentration curves of these amalgams show maxima at certain concentrations. These maxima are held to indicate some form of molecular aggregation (A. E. Dunstan and Thole, *Viscosity of Liquids* pp. 46).

### SUMMARY.

The experimental investigation is confined to the dilute liquid amalgams of the alkaline earth metals. The concentration ranges investigated are as follows:—

0.000 to 0.364 gms.	% of Barium,
0.000 to 0.4545 "	" " Strontium,
0.000 to 0.023 "	" " Calcium.

(1) The electrical conductivities and viscosities of Barium and Strontium amalgams suffer no change with time.

(2) The electrical conductivity of mercury decreases on the addition of Barium, and the electrical-conductivity-concentration curve of Barium amalgam exhibits discontinuities at the concentrations, 0.130, 0.225 and 0.325 gms. % of Barium. The electrical conductivities of Strontium and Calcium amalgams increase uniformly with concentration.

(3) The viscosity of mercury on the addition of Barium increases and viscosity-concentration curve of Barium amalgam exhibits maxima at the concentrations at which the discontinuities occur on the electrical-conductivity-concentration curve.

(4) The density of Barium amalgam decreases uniformly with concentration.

(5) The behaviour of dilute amalgams of the alkali and alkaline earth metals is examined in the light of different theories, particularly those of Skaupy and Lewis.

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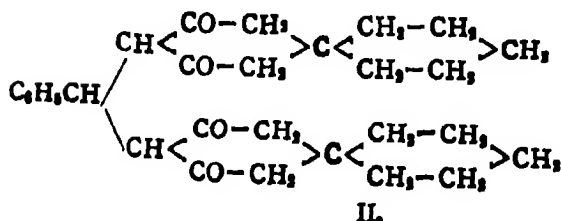
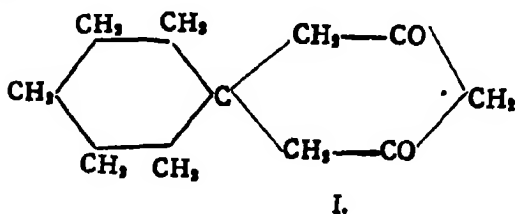
# DIHYDRORESORCINOLS PART III. THE CONDENSATION OF ALDEHYDES WITH CYCLOHEXANE-SPIRO-CYCLOHEXANE-3:5-DIONE.

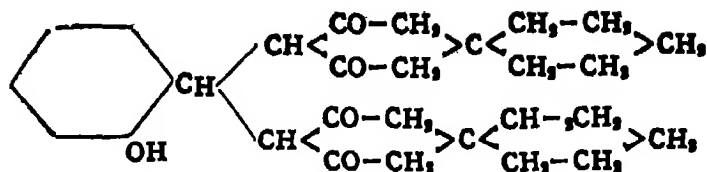
By

RANCHHODJI DAJIBHAI DESAI.

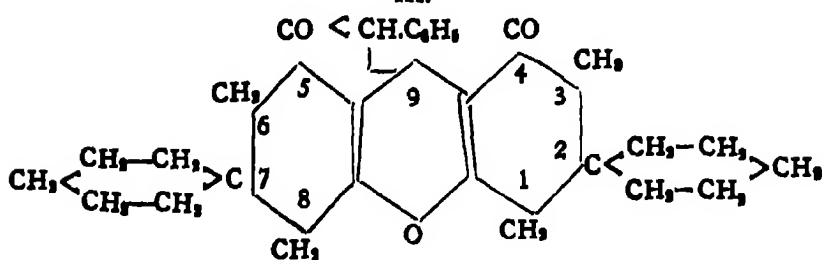
In continuation of the author's work on dihydroresorcinols [J.C.S.T. (1932), 1079 also in press.] it was thought interesting to condense the spiro compound, cyclohexane-spiro-cyclohexane-3 5-dione (I) with aldehydes in order to see how far its behaviour resembled that of dimethyldihydroresorcinol, as it has, sometimes, been observed that the derivatives of cyclohexane differ chemically from their dimethyl analogues. [Compare Desai J. C.S. (1932) 1081; Beesley Ingold and Thorpe, J.C.S. (1915), 1081; Qudrar-i-Khuda, J.C.S. (1929), 201.]

The action of benzaldehyde and salicylaldehyde on the dione (I) at the ordinary temperature, in presence of piperidine as a condensing agent, gave benzal-bis-cyclohexane-spiro-cyclohexane-3 5-dione (II) and salical-bis-cyclohexane-spiro-cyclohexane-3 5-dione (III). Under the influence of dehydrating agents like acetic anhydride, glacial acetic acid or gaseous hydrogen chloride, the compound (II) gave rise to 2-spiro-cyclohexane-4, 5-diketo-7-spiro-cyclohexane-9-phenyl-octahydroxanthene (IV). The dehydration of the salical derivative (III) can give rise to, either, the octahydroxanthene derivative (V) or the pyran derivative (VI).

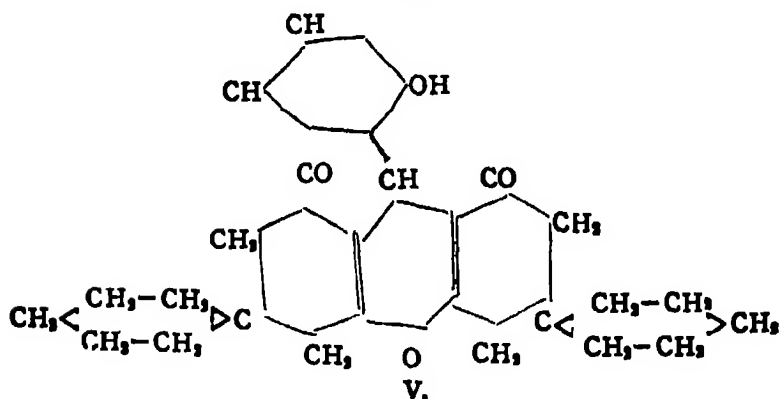




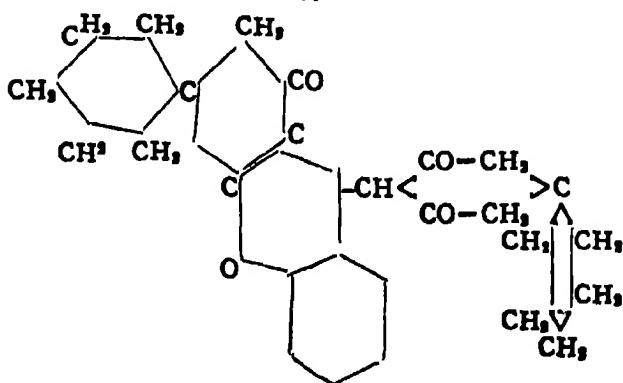
III.



IV.



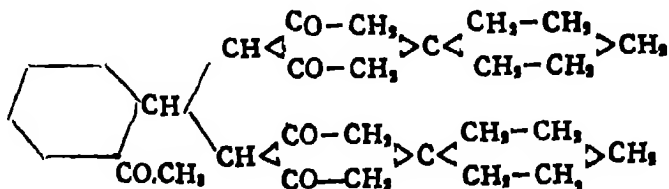
V.



VI.

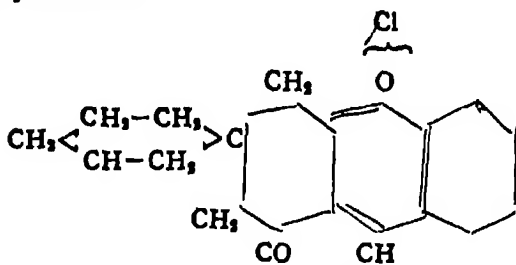
That the actual product formed is the octahydroxanthene derivative (V) is proved by the fact that when acetylsalicylaldehyde is con-

densed with the dione (I), the acetyl-salicyl-bis-cyclohexane-spiro-cyclohexane-3.5-dione (VII), which is first formed, undergoes dehydration to the xanthene derivative, which is formed by the acetylation of (V).

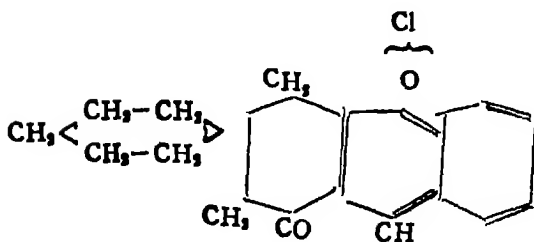


VII.

The Condensation of salicylaldehyde with the dione (I) in presence of gaseous hydrogen chloride as a condensing agent took a different course, and a scarlet compound was formed. This was found to be 2-spiro-cyclohexane-4-keto-tetrahydrobenzo-pyranol-anhydrochloride [(VIII) or (VIII)A]. Of the two alternative formulæ (VIII) or (VIII)A, the latter is preferred because the presence of the Ortho-quinonoid grouping in the benzene nucleus explains satisfactorily the colour of the anhydrochloride.



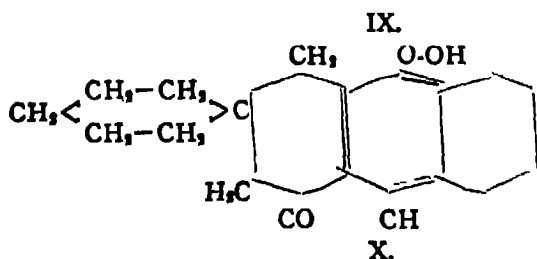
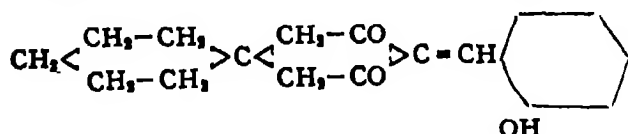
VIII.



VIII.A.

The formation of the anhydrochloride (VIII.A) must have involved the intermediate formation of salicylidene-cyclohexane-spiro-cyclohexane-3.5-dione (IX), but attempts to prepare it by the condensation of salicylaldehyde with the dione (I) either alone or under the influence of various alkaline as well as acid catalysts failed. Efforts were, then

made to prepare it by the alkaline hydrolysis of (VIII,A); but the anhydrochloride was found to be extraordinarily resistant to the hydrolytic action of Caustic alkali. The only product that could be isolated was the free base (X) corresponding to the anhydrochloride. Thus the behaviour of cyclohexane-spiro-cyclohexane-3.5-dione, was similar to that of dimethyldihydroresorcinol, so far as the condensation of benzaldehyde and salicyl-aldehyde was concerned.



### Experimental.

Cyclohexane-Spiro-cyclohexane-3.5-dione was prepared by the method of Norris and Thorpe [J. C. S. (1921), 1205]. When its alcoholic solution was treated with an excess of [40%] formaldehyde solution at ordinary temperature, *methylene-bis-cyclohexane-spiro-cyclohexane-3.5-dione* was immediately precipitated, and melted at 206° according to the above authors.

*2-Spiro-cyclohexane-4.5-diketo-7-spiro-cyclohexane-octahydroxanthene.* The above methylene derivative (1 g.) was heated with acetic anhydride (5cc.) on a free flame for 2 hours, and the excess of the anhydride decomposed by adding water. The precipitated solid was crystallised from dilute alcohol when white, prismatic needles melting at 215° were obtained. It was soluble easily in acetone, and glacial acetic acid, but sparingly in benzene (found C, 77.8; H, 8.6,  $\text{C}_{28}\text{H}_{30}\text{O}_8$ , requires C, 78.0; H, 8.47 percents).

#### (II) *Benzal-bis-cyclohexane-spiro-cyclohexane-3.5-dione.*

A mixture of benzaldehyde (2 g.), cyclohexanespiro-cyclohexane-3:5 dione (3.5 g), dry benzene (25 c.c.) and piperidine (4 drops) was kept at the ordinary temperature for 12 hours. The residue left after removing benzene under suction, was crystallised from dilute alcohol when lustrous needles melting at 132-133° were obtained. Its alcoholic solution gave red colouration with ferric chloride solution. (found C, 77.6, H, 8.1,  $\text{C}_{28}\text{H}_{30}\text{O}_4$ , requires C, 77.7, H, 8.0 percents).

*2-Spiro-cyclohexane-4'5-diketo-7-spiro-cyclohexane-9-phenyl-octahydroxanthene* (IV). When the above compound (1 g.) was heated with acetic anhydride (5 c.c.) on a free flame for 10-15 minutes, and the excess of the anhydride decomposed with water, a solid was precipitated. When crystallised from alcohol, the *octahydroxanthene* derivative was obtained in flat, prismatic needles, melting at  $188-189^{\circ}$ . This substance did not give any colouration with ferric chloride and was insoluble in Sodium Carbonate solution (found C, 80.6; H, 8.1;  $C_{29}H_{24}O_8$  requires C, 80.9, H, 7.9; percents).

*Salicyl-bis-cyclohexane-spiro-cyclohexane-3,5-dione* (III). A mixture of salicyl-aldehyde (2g), cyclohexane-spiro-cyclohexane-3,5-dione (3.5g), dry benzene (20 c.c.) and piperidine (4 to 5 drops) was left at the room temperature for 12 hours. The benzene was removed at the pump, and the solid crystallised from dilute alcohol, when white needles melting at  $185^{\circ}$  were obtained. It dissolved in Sodium Carbonate solution, and its alcoholic solution gave violet colouration with ferric chloride (found C, 74.9; H, 7.62;  $C_{29}H_{24}O_8$  requires C, 75.0, H, 7.76 percents).

*2-Spiro-cyclohexane-4'5-diketo-7-spiro-cyclohexane-9-O-hydroxy-phenyl-octahydro Xanthene* (V). The above compound (1gm.) was boiled with glacial acetic acid (15c.c.) for 3-4 hours, on dilution, white needles melting at  $193-194^{\circ}$  were obtained. This substance also gave violet colouration with ferric chloride and was soluble in sodium carbonate solution. It was also formed by saturating its absolute alcoholic solution with dry hydrogen chloride, and keeping the mixture overnight (found C, 77.7, H, 7.8;  $C_{29}H_{24}O_8$  requires C, 78.0 H, 7.6 percents).

The *acetyl derivative* was prepared by heating either the compound (III) or (V) with acetic anhydride for half an hour on a sand-bath. The excess of acetic anhydride was decomposed with water, and the solid crystallised from dilute alcohol, when prismatic needles melting at  $183-184^{\circ}$  were obtained. It did not give colouration with ferric chloride (found C, 76.1; H, 7.6;  $C_{31}H_{24}O_8$  requires C, 76.2; H, 7.5 percents).

*Acetylsalicyl-bis-cyclohexane-spiro-cyclohexane-3,5-dione* (VII). A mixture of acetylsalicyl aldehyde (1.2g.) cyclohexane-spiro-cyclohexane-3,5-dione (1.8g), dry benzene (10 c.c.) and piperidine (3 to 4 drops) was kept at ordinary temperature for 12 hours. The solid, left after the removal of benzene was crystallised from dilute alcohol, when white needles melting at  $190^{\circ}$  were obtained. Its alcoholic solution gave brown colouration with ferric chloride solution (found C, 73.4; H, 7.7;  $C_{31}H_{24}O_8$  requires C, 73.5, H, 7.5; percents).

When this compound was dehydrated by means of acetic anhydride or glacial acetic acid, the resulting product melted at  $183-184^{\circ}$ ,

and was identified as the acetyl derivative of (V), by means of mixed m. p.

*2-Spirocyclohexane-4-keto-tetrahydrobenzo-pyranol-anhydrochloride* (VIII, A). A solution of cyclohexane spiro-cyclohexane-3·5-dione (1g.), and salicylaldehyde (0·7g.) in methyl alcohol (10 c.c.) was saturated with a rapid current of dry hydrogen chloride at 0°. The solution became dark-red and viscous, and on keeping overnight, deep red crystals were deposited. These were filtered off, and washed on the filter paper with methyl alcohol saturated with dry hydrogen chloride. The substance did not melt below 300°, and began to decompose on exposure to moist air. It was sparingly soluble in usual organic solvents. The sample for analysis was dried in a vacuum over caustic potash (found C, 71·3, H, 6·4; Cl, 11·5, C<sub>18</sub> H<sub>18</sub> O<sub>2</sub> Cl requires C, 71·4; H, 6·28; Cl, 11·7; percents).

*The Anhydrobase* was prepared by adding sodium acetate solution to the warm solution of the anhydrochloride in a large excess of ethyl alcohol. The pale pinkish powder that was precipitated was filtered off, and washed alternately with water, alcohol, and ether. Sparingly soluble in almost all the organic solvents, the substance charred at about 300° without melting. The original deep-red colour of the anhydrochloride was restored if it was left in contact with methyl alcohol saturated with dry hydrogen chloride. The anhydrobase was recovered unchanged after heating with a concentrated solution of alcoholic caustic potash (found C, 75·8, H, 7·2; C<sub>18</sub> H<sub>20</sub> O<sub>3</sub> requires C, 76·0; H, 7·0 percents).

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# NITRIFICATION OF OIL CAKES IN THE TYPICAL SOILS OF THE BOMBAY PRESIDENCY

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## 1. *Introduction.*

Nitrogenous manures are important and their value is usually judged by the percentage of Nitrogen they contain but the real value of such a manure can be judged by the rate at which the nitrogen becomes available to the crop. Nitrogen is generally taken up by plants in the form of nitrates. The rate of nitrification may therefore be taken as a measure to find out the value of a nitrogenous manure. The rate of nitrification depends not merely on the nature of the organic matter but also on the nature of the soil to which the nitrogenous manure is applied. The value of the oil-cakes used as manure depends on the per cent. of nitrogen and also on the rate of nitrification. The latter may vary according to the nature of the soil.

In India nitrification of green manures has been worked by Joshi (1919) and the nitrification of oil-cakes like the Tili (sesamum orientale), Karanj (Ipomea glabra), Castor Linseed etc., on typical soils of Central Provinces and Berar was worked by Plymen and Bal (1919). They found that the rate of nitrification was different for different oil-cakes and for the same oil-cake it varied with the kind of soil. The object of the work described in this paper was to study the rate of nitrification of some important oil-cakes on the typical and important soils of the Bombay Presidency. The oil-cakes selected were the (1) Groundnut cake, (2) Castor cake and (3) Safflower cake and the soils used were the (1) Medium Black soil derived from the trap (Poona District), (2) Laterite soil from the Belgaum District and (3) the Goradu alluvial soil of the Kaira District.

The following figures indicate the nature of the soils,

TABLE NO. 1.

	Medium Black soil.	Laterite soil.	Goradu soil.
	%	%	%
Maximum water holding capacity.	48	38	20
Sticky point ( Moisture at )	26.4	16.7	6.4
Retentive portion.	66	49	28
Nonretentive portion.	34	51	72
Capillarity rise in Centimeters.			
3 hours.	2.5	7.5	12.1
3 days.	42.4	59.8	74.5
5 days.	70.1	80.1	80.2
8 days.	106.2	97.5	83.8
Loss on Ignition.	11.49	8.35	4.30
Lime ( CaO )	6.15	0.17	1.42

The composition of the oil-cakes used was as follows.

TABLE NO. 2.

	Safflower cake. Per cent.	Groundnut cake. Per cent.	Castor cake. Per cent.
Moisture.	9.95	3.62	4.55
	On oven dry matter		
Ether Extract.	4.59	10.53	5.13
*Albuminoids.	32.25	53.57	25.18
Woody fibre.	16.72	4.40	9.54
Other Carbohydrates.	29.21	23.53	49.97
*Containing Nitrogen.	5.16	8.57	4.03

## 2. Plan of Experiments.

In order to ensure even sampling of the oil cakes, a sample of each was passed through a handmill twice before it was taken for experiment. The uniformly ground sample was then sterilized in an Autoclave at 120°C. for an hour and then mixed with the soil.

Three sets for three different soils were arranged each containing five trays filled with 1000 grams of soil which was previously sampled and passed through 1 mm. sieve. Of the five trays the first received 3% Safflower cake, the second received 3% Groundnut cake, the third received 3% Castor cake and the fourth received a sample of 3% fat-



free Groundnut cake for comparative observations and to note if either the presence or absence of the high percentage of oil in the cakes affected the nitrifiability of the cakes. The fifth tray was the Control and received no cake.

Two more similar sets—one for the Laterite and the other for the Goradu soil—were filled up. A thorough mixing up was ensured by a number of nitrogen determinations from each of the trays.

At the start of the experiment moisture equivalent to 50% of the maximum water holding capacity of the respective soils (giving the optimum conditions of moisture) was added and evenly distributed by sampling. The loss of moisture due to normal evaporation was made up twice every week in order to maintain uniform moisture conditions. All trays were kept within a narrow limit of varying temperature namely between  $27^{\circ}$  and  $30^{\circ}\text{C}$ .

All the samples were analysed every fortnight and the following determinations were made :—

1. Nitrogen in all forms including
  - (a) Total nitrogen.
  - (b) Ammoniacal Nitrogen.
  - (c) Nitrate and Nitrite Nitrogen.

### 3. *Method of Analysis*

#### (a) *Total Nitrogen.*

20 grams of a sample soil was treated according to the Official Methods of Analysis (1921).

#### (b) *Ammoniacal Nitrogen.*

50 grams of the soil sampled was shaken with a solution of Sodium Chloride for half an hour and an aliquot portion of the extract was distilled over Magnesium Oxide and Ammonia was estimated as usual (McLean and Robinson (1924)).

#### (c) *Nitrate and Nitrite Nitrogen.*

The Griess Ilosway method for the determinations of nitrites and the Phenol Disulphonic acid method for the determinations of the nitrates were employed. In both cases the standard Tinto-meter glasses were used for matching the developed colour.

It was found that the extracts of the samples with Groundnut cake were turbid on account of the fine suspended matter and the extracts with Safflower cake were coloured yellow. This interfered

with the estimations and therefore the following method suggested by Syme (1909) was used to remove the difficulty:—

About 50 c.c. of the soil extract was heated to about 50° to 60°C. and treated with 1 c.c. of dilute (1 to 5) Sulphuric acid followed by an excess of Potassium permanganate (5 to 10 grams dissolved in a litre) which is added from a burette. The extract is heated for 15 minutes on a water bath, more Potassium permanganate solution being added from time to time if required. The whole is filtered and the filtrate made slightly alkaline with Sodium Carbonate and evaporated to dryness on a water bath. The residue is taken up with water and filtered and the filtrate is made up to 50 c.c. and the Nitrates estimated as usual. In such a case the nitrites originally present turned into nitrates.

#### 4. *Nitrogen Changes of Oil Cakes in Soils.*

Of all the chemical changes that take place during the process of nitrification of the nitrogenous organic matter in the soil, ammonification marks a very definite and readily perceptible change. The estimation of ammoniacal nitrogen of the samples at regular intervals of time would give a fair idea with regard to the comparative rates of decomposition of the samples of oil-cakes used in the experiment. The three different sets with the three different soils have given appreciably different results and therefore it is proposed to examine them separately.

In all 8 determinations at regular stages were made including the observations at the start and extending over a period of 100 days.

##### (a) *Medium Black Soil.*

TABLE NO. 3.

Milligrams of ammoniacal nitrogen per 100 grams of oven dry soil.

Time.	Groundnut Cake. Ordinary.	Groundnut Cake. Fat-Free.	Safflower. Cake.	Castor Cake.	Control
0 days.	0.51	0.53	Trace.	Trace.	Trace.
14 days.	6.12	5.86	2.70	2.41	0.45
28 days.	11.19	10.38	5.00	4.54	0.94
42 days.	16.40	15.34	8.08	7.28	1.24
56 days.	28.23	26.21	12.45	11.60	1.64
70 days.	49.72	37.56	18.26	16.31	1.59
84 days.	71.39	47.13	21.91	22.18	1.62
100 days.	92.21	64.35	26.65	27.40	1.51

The figures presented in the above table show clearly enough the different degrees of ammonification in the different samples of oil cakes used. Taking the Groundnut cake, we find the ammoniacal nitrogen content of the sample is increased day after day until at the end of 100 days, 92 milligrams of ammoniacal nitrogen is found per 100 grams of oven dry soil. If we examine the figures for all different stages at which the samples were analysed it can be seen that there is a gradual rise in the ammoniacal nitrogen contents throughout.

In the case of the fat-free Groundnut cake the ammonification is appreciably lower than the ordinary cake. This suggests that either the removing of fat results in the lowering of the rate of decomposition or that the extraction of the fat by Ether might have affected an anti-biotic condition if ammonification is regarded as a bio-chemical change. Playmen and Bal (1919) have not found the fat-free Tili cake inferior to the ordinary cake in their experiments where they seem to have made a comparative study of the ordinary Tili cake and the fat-free Tili cake as has been done in the case of Groundnut cake in these experiments. The comparative study made here suggests that the process of ammonification is not a purely chemical process. If it were so there should not have been so much difference in the ammonifiability of the ordinary Groundnut cake and the fat-free Groundnut cake because these two samples are under precisely identical conditions otherwise. Taking also the view that ammonification is an autocatalytic change we find that both the samples had a fairly equal start and the differences brought about in the later stages were due to other non-chemical influences. There is a very important suggestion made by Subramhayan (1925) that ammonification is an enzyme action. It is quite probable from this point of view that the enzymes present in the Groundnut cake were either destroyed in the process of extraction by Ether or were extracted along with the fat.

Considering next the figures obtained in the case of the Safflower cake and the Castor cake it can be seen that both of them are slow and compete closely in the extent of decomposition. The Safflower cake is richer in nitrogen content by 1% than the Castor cake but is slightly slower in ammonification because it contains 16% woody fibre as against 9% in the Castor cake (Table No. 1). The Groundnut cake of course contains the lowest amount of woody fibre being only 4% which also speaks in favour of its rapid decomposition.

In presenting the nitrification figures they are given as nitrogen nitrified per 100 grammes of the original total nitrogen present in the various samples, because these figures would be easily comparable although the percent of nitrogen may be different in different oil-cakes.

TABLE NO. 4.

( Nitrification of various oil cakes. )

Nitrified nitrogen per 100 grammes of the total nitrogen present.

Time.	Groundnut Cake. Ordinary.	Groundnut cake. Fat-free.	Safflower cake.	Castor cake.	Control
0 days.	0.55	0.52	0.43	0.46	0.50
14 days.	2.42	1.74	2.10	2.14	1.12
28 days.	5.13	3.96	4.35	4.98	1.54
42 days.	9.44	6.72	6.38	8.08	2.19
56 days.	17.26	10.52	8.62	11.44	2.83
70 days.	25.52	16.81	12.10	16.28	3.21
84 days.	33.64	27.20	16.22	20.24	3.22
100 days.	41.82	34.40	20.10	24.33	3.19

A glance at Table No. 3 shows the different degrees of nitrification of the different oil cakes. They stand just in the same order as they stood in the ammonification process and therefore there are reasons to suppose that there is some inter-depending connection between ammonification and nitrification although Lipham and Burges (1917) say that —

“The ammonifiability data of fertiliser nitrogen in soils are not useful indication of nitrifiability data on the same fertiliser and on the same soil.”

Thus 41% of the total nitrogen in the ordinary Groundnut cake is nitrified in a period of 100 days while only 34% of the total nitrogen in the fat-free Groundnut cake is oxidised within the same period. Even if the Blanks which are common to all the samples are deducted the comparative value remains the same. It is again indicated here that either the extraction of oil cake or the method of extraction inhibits the process of nitrification.

The Safflower cake is as slow in nitrification as it was in the ammonification and only 20% of its total nitrogen is nitrified. The Castor cake nitrifies to the extent of 24% and therefore supplies a little more available nitrogen than the Safflower cake.

#### (b) Laterite Soil.

The same samples of oil cakes show a marked difference both in ammonification and nitrification in the Laterite soil. The following table makes this clear,

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TABLE NO. 5.

Ammonification of various oil cakes in the Laterite soil.  
Milligrams of ammoniacal nitrogen per 100 grams of oven dry soil.

Time.	Groundnut Cake. Ordinary.	Groundnut Cake. Fat-free.	Safflower Cake.	Castor Cake.	Control
0 days.	0.49	0.51	Trace	Trace	Trace.
14 days.	2.31	1.88	0.86	0.66	Trace.
28 days.	8.86	6.54	2.46	2.23	0.29
42 days.	15.54	12.18	5.17	4.87	0.40
56 days.	24.28	18.30	7.79	7.63	0.38
70 days.	33.16	23.82	10.11	10.42	0.37
84 days.	41.82	29.04	13.26	14.80	0.44
100 days.	49.45	34.70	15.40	17.40	0.36

Here the ammonifiability is far lower than that obtained in the Medium Black soil. This is another reason to support the view that the process of ammonification is neither purely chemical nor is it purely an enzymic action. If it were purely a chemical one the same condition of moisture and time would have given the same amount of ammonification even in this soil. Even if it were an enzymic action, all the samples except the fat-free Groundnut cake had the enzymes safe and they would act in this soil as well. These observations do hint that the soil exerts a very considerable influence on the ammonification as well as nitrification and this influence is in all probability a bio-chemical one.

The general figures in the above table leave no doubt that the Laterite soil is biologically very poor or at least poorer than the Medium Black soil.

Even in the case of nitrification the figures in this soil are very low and the samples stand in the same order as in the case of ammonification.

TABLE NO. 6.

Nitrification of various oil cakes in the Laterite soil.  
Percent of nitrified nitrogen of the total nitrogen present.

Time.	Groundnut Cake. Ordinary.	Groundnut Cake. Fat-free.	Safflower Cake.	Castor Cake	Control.
0 days.	0.45	0.31	0.21	0.38	0.23
14 days.	1.83	2.01	1.58	1.67	0.27
28 days.	4.54	4.77	2.86	3.06	0.26
42 days.	8.22	8.87	5.19	5.48	0.28
56 days.	13.76	12.79	8.80	8.93	0.36
70 days.	19.04	16.81	13.09	13.42	0.31
84 days.	24.39	20.95	16.56	17.02	0.28
100 days.	29.57	25.65	18.96	20.40	0.28

The ordinary Groundnut cake nitrifies only to the extent of 29% of its total nitrogen, while the fat-free Groundnut cake nitrifies to the extent of 25%. The corresponding nitrification figures in the Medium Black soil are 41% and 34% respectively, showing a large drop in nitrification. The Safflower cake and the Castor cake are close to each other as in the Medium Black soil, the Castor cake being slightly better than the Safflower cake. The woody fibre in the Safflower cake is clearly a handicap in its nitrification.

(c) *Goradu Soil.*

The same oil cakes added to the Goradu soil showed interesting results. The Goradu soil is distinctly superior to the Laterite soil although it stands below the Medium Black soil. The idea that the lime content of the soil and its biological activity has some correlation gains support from these results. The lime percent in Goradu soil is double that of Laterite soil. The following table presents figures on the ammonification of oil cakes.

TABLE NO. 7.

( Ammonification of various oil cakes in the Goradu soil ).

Milligrams of ammoniacal nitrogen per 100 grams of oven dry soil.

Time.	Groundnut cake. Ordinary.	Groundnut cake. Fat-free.	Safflower cake.	Castor cake.	Control.
0 days.	0.32	0.31	Trace	Trace	Trace
14 days.	3.18	1.83	0.82	0.54	0.34
28 days.	7.41	4.71	1.43	1.03	0.42
42 days.	14.36	9.36	4.56	3.23	0.51
56 days.	23.53	14.52	8.89	5.16	0.52
70 days.	36.19	24.41	14.38	11.20	0.49
84 days.	47.45	32.12	18.92	16.28	0.43
100 days.	58.26	40.80	24.14	19.82	0.36

The ammonification is fairly rapid in this soil though by no means equal to that in the Medium Black soil. The fat free Groundnut cake is found to be distinctly inferior material throughout the experiments with all the types of soil. The only point of importance here is that the Safflower cake is better than the Castor cake in this soil in spite of its high woody fibre content.

A comparative table for all the soils showing the extent of ammonification after 100 days gives a better idea,

TABLE NO. 8

( Comparative study of ammonification of various oil cakes in the three different soils.)

Milligrams of ammoniacal nitrogen per 100 grams of oven dry soil.

Time	Groundnut cake. Ordinary.	Groundnut cake. Fat-free.	Safflower cake.	Castor cake.	Control.
<i>The Medium Black Soil.</i> 100 days.	92 21	64.35	26 65	27 40	1.51
<i>The Laterite Soil</i> 100 days.	49.45	34 71	15.40	17.40	0.36
<i>The Goradu Soil</i> 100 days.	58 26	40.80	24.14	19.82	0.36

The figures on nitrification are also interesting because they prove the superiority of the Goradu soil over the Laterite soil. The Safflower cake is more suitable than the Castor cake for the Goradu soil is again confirmed by the figures on the nitrification as under.---

TABLE NO. 9

( Nitrification of various oil cakes in the Goradu soil. )

Percent of nitrified nitrogen of the total nitrogen present.

Soil and Time	Groundnut cake. Ordinary	Groundnut cake. Fat-free	Safflower cake.	Castor cake.	Control.
0 days.	0 32	0 41	Trace	Trace	Trace
14 days.	1 40	1 24	0.72	0 38	0.26
28 days.	3 68	2 93	1 62	1.38	0.38
42 days.	8 29	6 83	3 46	2 53	0.41
56 days.	14 13	12 54	6 29	5.18	0.47
70 days.	20.75	18.22	12 30	12.62	0.39
84 days.	27.17	24 04	15 82	17 30	0.34
100 days.	32 95	29 82	19 52	17.30	0.36

A comparative table for the nitrification of all the oil cakes after a period of 100 days could be presented as follows :—

TABLE No. 10.

(Comparative study of nitrification of various oil cakes in different soils.)

Percentage of total nitrogen nitrified.

Soil.	Groundnut cake. Ordinary.	Groundnut cake. Fat-free.	Safflower cake.	Castor cake.	Control.
The Medium Black.	41.82	34.40	20.10	24.33	3.19
The Laterite	29.57	25.65	18.96	20.40	0.28
The Goradu	32.95	29.82	19.52	17.30	0.36

Thus the study of the nitrification of the different oil cakes in the different soils shows the marked differences in the availability of nitrogen of the various materials added to the soil and at once gives us the idea about the efficiency of the material added as manure. This also clearly shows that merely a high percentage of nitrogen in a substance does not mean much if the rate of its availability is not known. Similarly the experiments show also the marked difference in the soils, and suggest that the biological activity of the soils is perhaps a more important factor than the physical and the chemical properties.

5. The results so far examined could be summarised as follows :—

1. The Groundnut cake is the most easily nitrifiable material of the oil cakes used in the experiments.

2. The fat-free Groundnut cake is distinctly inferior in nitrification than the ordinary Groundnut cake.

3. The Safflower cake and the Castor cake compete very closely and if a comparison has to be made, the Castor cake nitrifies better than the Safflower cake in the Medium Black soil and the Laterite soil while the Safflower cake stands better in the Goradu soil.

4. Ammonification and nitrification show a close relation.

5. Of the soils examined the Medium Black soil is the most active. The Goradu soil comes next and the Laterite soil stands last.

6. *The Loss of Nitrogen.*

Although under an anaerobic conditions there is no loss of nitrogen during the process of decomposition according to Subramahanyan (1927) we find that this is by no means the case under aerobic conditions. Joshi (1919) observed such a loss during the study of biochemical decomposition of Cowdung and Urine, and remarked :—



"Under aerobic conditions there was loss in all cases but as the figures for the loss of moisture under these conditions were not accurately determined before hand no opinion can be expressed as to the relative loss of nitrogen from each of the materials."

But at another place the same worker remarks that he did not find any loss of nitrogen in the decomposition of organic matter.

A remarkable loss of nitrogen has been found during the experiments on the nitrification of oil cakes so far examined. The loss varied with the nature of the oil cakes as well as with the nature of the soil. The following table gives the figures of total nitrogen as obtained at various stages of nitrification in the Medium Black soil :—

TABLE No. 11.

The total nitrogen of various oil cakes at different stages of nitrification.

Milligrams per 100 grams of oven dry soil.

Days.	Groundnut cake. Ordinary.	Groundnut cake. Fat-free.	Safflower cake.	Castor cake.	Control.
0 days.	413	443	314	280	169
14 days.	412	443	315	278	169
28 days.	413	440	313	279	168
42 days.	409	441	312	276	168
56 days.	408	440	310	273	168
70 days.	402	438	310	273	168
84 days.	382	436	308	271	167
100 days.	364	434	304	269	167
<i>Net Loss.</i>	49	9	10	11	2

The loss of nitrogen in the ordinary Groundnut cake sample is the greatest. As many as 48 milligrams are lost in a period of 100 days. Other oil cakes lose comparatively small quantities. Thus the Safflower cake loses only 10 milligrams and the Castor cake 11 milligrams during the same period. The control loses only 2 milligrams. The fat-free Groundnut cake shows particularly interesting results inasmuch as it loses only 9 milligrams showing the smallest loss. The reason for the loss of total nitrogen is probably the process of denitrification that always goes on in the soil when nitrates accumulate to a certain limit as explained by Warrington (1892). If denitrification is also a bio-chemical change, the removal of oil from the Groundnut cake retards this activity also.

The loss of nitrogen is different with different soils. The lighter the soil the greater the loss. The following table gives the total nitrogen as obtained in the Laterite soil at various stages :—

TABLE NO. 12.

The total nitrogen of various oil cakes at different stages of nitrification in the Laterite soil.

Milligrams per 100 grams of oven dry soil.

Days.	Groundnut cake. Ordinary.	Groundnut cake. Fat free.	Safflower cake.	Castor cake.	Control.
0 days.	358	388	284	224	117
14 days.	358	388	285	225	118
28 days.	351	386	285	225	117
42 days.	356	387	284	224	117
56 days.	342	384	282	220	116
70 days.	338	378	279	216	117
84 days.	321	374	274	215	116
100 days.	303	373	272	215	116
Net loss	55	15	12	9	1

The increased loss in the Groundnut cakes amplies is conspicuous in the Laterite soil. The other samples do not show much difference as compared to the Medium Black soil.

The figures for total nitrogen in the Goradu soil confirm the observation made above. The figures are presented in the following table .—

TABLE NO. 13.

The total nitrogen of various oil cakes at different stages of nitrification in the Goradu soil.

Milligrams per 100 grams of oven dry soil.

Days.	Groundnut cake. Ordinary.	Groundnut cake. Fat-free.	Safflower cake.	Castor cake.	Control.
0 days.	290	320	180	158	48
14 days.	290	320	181	158	48
28 days.	289	319	181	156	47
42 days.	285	318	178	157	48
56 days.	278	316	179	154	47
70 days.	268	308	178	154	46
84 days.	252	302	176	150	46
100 days.	225	300	174	150	46
Net loss.	65	20	6	8	2

A comparative study of the different soils and different samples of oil cakes will give a clear idea for which the following table will be useful :—

TABLE NO. 14.

( A comparative study of the loss of nitrogen in different soils with different oil cakes. )

Milligrams of total nitrogen lost per 100 grams of oven dry soil in a period of 100 days.

Soil.	Groundnut cake. Ordinary.	Groundnut cake. Fat-free	Safflower cake.	Castor cake.	Control.
The Medium Black.	48	9	10	11	2
The Laterite.	55	15	12	9	1
The Goradu.	65	20	6	8	2

Thus the loss of nitrogen in the Groundnut cake is found to be the greatest in all the soils. If soils are compared, the Goradu soil loses comparatively more nitrogen than the Medium Black and the Laterite soils.

The loss is chiefly found to be considerable when large quantities of nitric nitrogen begin to accumulate.

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ACTION OF ACETIC ANHYDRIDE AND SODIUM ACETATE  
ON THE ANHYDRIDES OF  $\beta$ -ARYL-GLUTACONIC  
ACIDS —  
FORMATION OF GLUTACONYL-ACETIC ACIDS.

*By*

DATTATRAYA BALKRISHNA LIMAYE AND VISHNU MAHADEV BHAVE

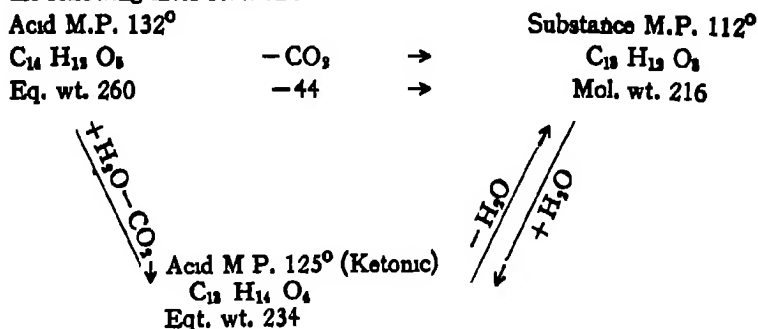
*Introduction —*

Based on an earlier observation by one of us a simple method has been developed in this laboratory of preparing a number of  $\beta$ -aryl-glutaconic acids and the formation of the corresponding anhydride in a typical case of  $\beta$ -(4-methoxy-phenyl)-glutaconic acid has been described in the Journal of the Indian Chemical Society 1931, 8,139. This anhydride titrates with alkali as a monobasic acid and gives a colouration with ferric chloride. In order to account for similar properties of the substituted glutaconic anhydrides studied by Thorpe and Collaborators, an hydroxy anhydride structure, as distinguished from the "normal," has been suggested by them and acetyl derivatives have been prepared by the action of acetyl chloride on the OH group in some of the cases (J. Chem Soc 1911, 99, 2187; 1912, 101, 858). With a view to prepare a similar neutral acetyl derivative the action of acetic anhydride was first tried on the  $\beta$ -(4-methoxy-phenyl)-glutaconic anhydride. It was soon observed however that acetic anhydride alone had no action, but that in the presence of fused sodium acetate products were obtained which proved to be different from the expected neutral acetyl derivative. Further investigation has led to the discovery of glutaconyl acetic acids and related compounds, which form the subject of the present communication.

*Theoretical .—*

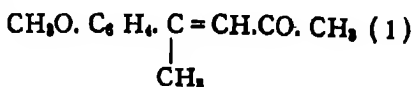
The product obtained from  $\beta$ -(4-methoxy-phenyl)-glutaconic acid by the action of acetic anhydride and sodium acetate under conditions described in the experimental part, melted between 115° to 125°C and was obviously a mixture. Three substances were ultimately separated from this an acid M.P. 132°C forming the main product, a neutral product M.P. 112°C and a ketonic acid M.P. 125°C. Out of these only the acid M.P. 132° gave a colouration with ferric chloride. The substance M. P 112° resulted from the acid M.P. 132° by the loss of one molecule of CO<sub>2</sub>. It thus became clear that, the nature of the reaction was not that of the acetylation of the colour giving OH of the anhydride of the glutaconic acid.

A closer study of the properties of the three substances revealed the following inter-relation :—



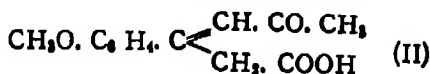
This indicated that the acid M.P. 132° was the primary product of the reaction and the other two substances were by-products. It appeared probable that the substance M.P. 112° was a lactone of the ketonic acid M.P. 125° and that the substance M.P. 132° was a lactic acid. It was therefore decided to determine the structure of the ketonic acid M.P. 125° first

When heated above its melting point the ketonic acid gave a neutral ketone  $C_{13} H_{14} O_2$  M.P. 48°, by loss of  $CO_2$ . This ketone on oxidation with chromic acid gave anisic acid, a fact which did not throw much light on the constitution. However when oxidised by Iodine in alkaline solution an acid  $C_{11} H_{12} O_4$  M.P. 155° was obtained which was identified as paramethoxy- $\beta$ -methyl-cinnamic acid. This fixed the structure of the ketone M.P. 48° as (4-methoxy- $\alpha$ -methyl) benzylideneacetone or in other words— $\alpha$ -acetonyl  $\alpha$ -(4-methoxy-phenyl)-ethane.



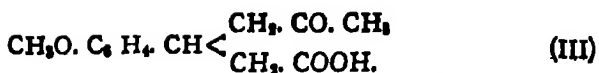
The oxidation reaction is similar to that of benzylideneacetone to cinnamic acid by alkaline hypochlorite.

The structure of the Ketonic acid M.P. 125° could now be represented as

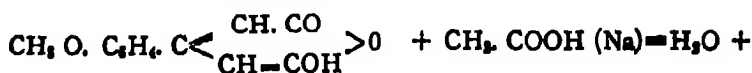


The alternative structure  $CH_3O.C_6H_4.C \begin{cases} \nearrow CH.CO.CH_3.CO.OH \\ \searrow CH_3 \end{cases}$

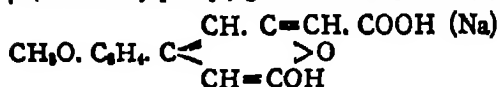
was set aside as the properties of the acid did not accord with those of a  $\beta$ -Ketonic acid and the formation of a lactone, not containing a carbonyl group could not be explained. Moreover the structure of the keto acid is confirmed, as on reduction it passes into  $\beta$ -(4-methoxy-phenyl)- $\gamma$ -aceto-butyric acid which is a known substance,



Hence the action of acetic anhydride and sodium acetate on  $\beta$ -(4-methoxy phenyl)-glutaconic anhydride can be represented as,

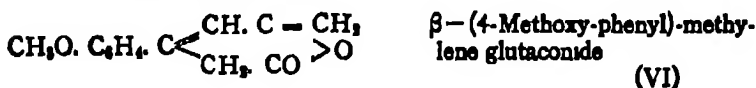


$\beta$ -(4-Methoxy-phenyl)-glutaconic anhydride (hydroxy form) (IV)



$\beta$ -(4-Methoxy-phenyl)-glutaconyl-acetic acid (V)

The glutaconyl-acetic acid then gives, by decarboxylation the neutral substance M. P.  $112^\circ$



The corresponding 'Normal' or 'keto' form of the glutaconyl-acetic acid has also been isolated. Regarding this as also the effect of conjugation on the course of the reaction, will be reported in a future communication.

The reaction has been extended to five other glutaconic anhydrides.

It will be seen that the reaction resembles Perkin's reaction for unsaturated acids of the cinnamic type or to be more correct the Gabriel's extension of Perkin's reaction to phthalic anhydride (Berichte 1893, 26, 952, 1896, 29, 2518). The parallelism is so close that it can be followed through almost the entire series of related compounds viz.

(1)	(2)	(3)
(a) Phthalic anhydride.	Phthalyl-acetic acid.	Methylene phthalide.
(b) Glutaconic anhydride	Glutaconyl-acetic acid.	Methylene-glutaconide.
(4)	(5)	(6)
(a) Dibasic $\beta$ Ketonic acid.	Acetophenone ortho-carboxylic acid.	Acetophenone.
(b) Unstable $\beta$ ketonic dibasic acid (not isolated).	$\beta$ -4-Methoxy-phenyl- $\gamma$ -aceto-vinylacetic acid.	Methylbenzylidene acetone.

**Experimental :—**

(1) *Isolation of the three products* formed by the action of acetic anhydride and sodium acetate on  $\beta$ -(4-methoxy-phenyl)-glutaconic anhydride. (IV)

As the  $\beta$ -aryl-glutaconic acids are readily converted into the anhydrides by the action of acetic anhydride, it was found possible to use the acids themselves as starting material, provided sufficient acetic anhydride was used for the reaction.

A mixture of 5 grms. of  $\beta$ -(4-methoxy-phenyl)-glutaconic acid. 5 grms. of fused sodium acetate and 7.5 c.c. of acetic anhydride is heated at the temperature of boiling water bath for 7 to 10 minutes. The resulting red liquid is poured in 100 c.c. of water, stirred and allowed to stand for two hours. A brittle cake separates, it is removed by filtration and on purification yields an acid M. P.  $132^{\circ}$  (yield 3 grms.). On leaving the filtrate over night a second crop of reddish crystals is obtained, separable by boiling water into an acid M. P.  $125^{\circ}$  (0.4 grams) and a neutral substance M. P.  $112^{\circ}$  (0.3 gm.). The last two substances are more conveniently prepared from the acid M. P.  $132^{\circ}$ , the following modification serves as a preparative process for the acid M. P.  $132^{\circ}$ .

(2)  $\beta$ -(4-Methoxy-phenyl)-glutaconyl-acetic acid M. P.  $132^{\circ}$  (V)

After pouring the melt in water as described above about 8 c.c. of hydrochloric acid (1.16) are added. The sticky mass that solidifies in about an hour is filtered off and washed. It can be purified by crystallisation from glacial acetic acid or alcohol. Best results are obtained by exactly neutralising with normal caustic soda, filtering and precipitating the filtrate by the addition of 10 normal caustic soda, collecting the sodium salt, washing it with small amounts of water and regenerating the acid by hydrochloric acid, and crystallising it from 75% acetic acid. The acid thus obtained melts at  $132^{\circ}$  without decomposition. In alcoholic solution the acid gives a strong violet colouration with ferric chloride. It is insoluble in water, sparingly soluble in dilute acetic acid, alcohol, acetone, and benzene, and soluble in ether.

Found C = 64.5 ; H = 4.6 Equivalent = 261

$C_{14}H_{12}O_6$  requires C = 64.6 ; H = 4.6 „ = 260

It gives paramethoxy acetophenone on boiling with 15% caustic alkali.

(3)  $\beta$ -(4-Methoxy-phenyl)- $\gamma$ -aceto-vinylacetic acid (II)

A clear solution of the glutaconyl acetic acid M. P.  $132^{\circ}$  5 grms. dissolved in 125 c.c. normal caustic alkali is allowed to stand over night and then warmed on water bath for half an hour, cooled, extracted with ether to remove some oily impurities and acidified with dilute



hydrochloric acid, keeping the solution cool. The solid that separates is somewhat sticky and its purification requires care. It is first crystallised from 75% acetic acid and then from hot water avoiding long boiling. The perfectly white crystals melt at  $125^{\circ}$  with decomposition. Found C = 66.3, H = 6.15 % Equivalent = 233

$C_{13}H_{14}O_4$  requires C = 66.6, H = 6.0 % Equivalent = 234

The acid gives no colouration with ferric chloride. It is soluble in ether, benzene, chloroform acetone and alcohol, and sparingly soluble in acetic acid and water.

The semicarbazone of the acid melts at  $155^{\circ}$  with decomposition and titrates as a monobasic acid. Found equivalent 293.  $C_{14}H_{17}O_4N_3$  requires equivalent 291.

The Phenyl hydrazone of the acid melts at  $165^{\circ}$  with decomposition. Found equivalent 325.  $C_{19}H_{20}O_3N_2$  requires equivalent 324.

The Oxime melts at  $190^{\circ}$  with decomposition.

The ethyl and methyl esters of the acid cannot be prepared by the Fischer-Spier method as the formation of the lactone M. P.  $112^{\circ}$  is favoured. The same can however be prepared through the silver salt by the action of alkyl iodides, but cannot be purified, as even distillation in vacuum gives the lactone.

#### (4) $\beta$ (4-Methoxy-phenyl)-methylene glutaconide (VI)

This lactone of  $\beta$ -(4-methoxy phenyl)- $\gamma$ -aceto-vinylacetic acid can be obtained as described in Exp 1, or by the action of acetic anhydride on the ketonic acid. It is best prepared by heating 5 grms. of the glutaconyl-acetic acid with 10 c.c. of 30% hydrochloric acid over a sand bath for 2 hours and pouring the resulting solution in water. The solid that separates is filtered off, treated with cold dilute alkali, filtered, washed with water, and finally crystallised from alcohol. The beautiful plates with pearly lustre melt at  $112^{\circ}$  yield 2.3 grms.

Found C = 72.0, H = 5.7%

$C_{13}H_{12}O_5$  requires C = 72.2, H = 5.6%

It gives no colouration with ferric chloride. It is insoluble in water and dilute acetic acid, sparingly soluble in alcohol, glacial acetic acid and benzene, and soluble in ether and chloroform. On hydrolysis with alkali it gives the  $\delta$ -Keto acid M.P.  $125^{\circ}$ . It does not react with ketonic reagents.

#### (5) (4-Methoxy- $\alpha$ -methyl-benzylidene)-acetone (I)

The acid M. P.  $125^{\circ}$  (Exp.3) is heated above its melting point till the evolution of  $CO_2$  ceases and then distilled under reduced pressure.

A liquid passes over at  $145^{\circ}$  at 5 m.m. pressure. It is purified by redistillation when a neutral solid M.P.  $48^{\circ}$ , is obtained.

Found  $C = 75.5$ ;  $H = 7.6\%$

$C_{13}H_{14}O_2$  requires  $C = 75.8$ ;  $H = 7.3\%$

*The Semicarbazone* M.P.  $193^{\circ}$

Found  $C = 63.3$ ;  $H = 6.8\%$

$C_{13}H_{17}O_2N_2$  requires  $C = 63.2$ ,  $H = 6.9\%$

*The Phenylhydrazone* M.P.  $70^{\circ}$  *The Oxime* M.P.  $107^{\circ}$

*Oxidation of the Ketone* —A mixture of 2 grms of the ketone M.P.  $48^{\circ}$  and 25 c.c. of 4 normal caustic alkali is shaken for an hour with the addition of 9 grms. of Iodine, allowed to stand for 3 hours, treated with sodium sulphite, acidified and left over night. The crystals that separate, on purification, melt at  $154^{\circ}$  to  $155^{\circ}$ .

Found  $C = 68.8$ ,  $H = 6.1\%$ , Equivalent = 192

$C_{11}H_{13}O_3$  requires  $C = 68.76$ ,  $H = 6.25\%$ , „ = 192

This acid was identified as paramethoxy  $\beta$ -methyl-cinnamic acid by mixed melting point with the known compound and by its conversion into the known paramethoxy-iso-propylene benzene

(6)  $\beta$ -(4-Methoxy-phenyl)- $\gamma$ -aceto butyric acid (III)

$\beta$  (4-Methoxy phenyl)- $\gamma$ -aceto-vinylacetic acid (10 grms) is neutralised with dilute caustic soda and reduced with the slow addition of 100 grms. of 4 % sodium amalgam. After 2 hours the solution is filtered, acidified and the separated acid purified by crystallisation first from water and then from dilute acetic acid. The acid melts at  $104^{\circ}$  and can be distilled under reduced pressure

Found  $C = 66.0$ ,  $H = 6.6\%$  Equi = 235

$C_{13}H_{16}O_4$  requires  $C = 66.1$ ,  $H = 6.8\%$  „ = 236

The acid was identified as the known  $\beta$  (4-methoxy phenyl)- $\gamma$ -aceto-butyric acid by preparing the semicarbazone M. P.  $190^{\circ}$ , the Oxime M. P.  $169^{\circ}$  (Vorlander, *Annalen* 1896, 294, 253,) and the ethyl ester B. P. at 5 m.m.  $190^{\circ}$  to  $195^{\circ}$ , which in turn was converted by sodium ethoxide into anisyl dihydro resorcin a known compound (Vorlander, l. c.).

The reaction has been extended to five other  $\beta$ -Aryl glutaconic acids and the various products obtained by similar methods resemble in properties with corresponding compounds described above. They are assembled in the following table.

S. No.	Substance	B P M P °C	Formula	Analysis	
				found	required
1.	<i>β</i> -Aryl-glutaconyl-acetic acids				
2.	4-Methoxy-3-methyl-phenyl-	M. P. 189	C <sub>15</sub> H <sub>14</sub> O <sub>5</sub>	C=65.5, H=5.0	C=65.7, H=5.1%
3.	2-Methoxy-5-methyl-phenyl-	M. P. 129	C <sub>15</sub> H <sub>14</sub> O <sub>5</sub>	C=65.5, H=4.9	C=65.7; H=5.1%
4.	Phenyl-	M. P. 115	C <sub>15</sub> H <sub>10</sub> O <sub>4</sub>	C=67.6, H=4.2	C=67.8, H=5.3%
5.	2-Methoxy-4-methyl-phenyl-	M. P. 138	C <sub>15</sub> H <sub>14</sub> O <sub>5</sub>	C=65.6, H=5.1	C=65.7, H=5.1%
	2-Methoxy-phenyl-	M. P. 116	C <sub>14</sub> H <sub>12</sub> O <sub>5</sub>	C=64.7, H=4.5	C=64.6; H=4.6%
6.	<i>β</i> -Aryl-T-acetovinylacetic acids				
7.	4-Methoxy-3-methyl-phenyl-	M. P. 146	C <sub>14</sub> H <sub>12</sub> O <sub>4</sub>	C=67.5, H=6.4	C=67.7, H=6.5%
8.	Semicarbazone of (6)	M. P. 155	C <sub>15</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub>	Equivalent 303	Equivalent 305
9.	Phenyl-hydrazone of (6)	M. P. 165	C <sub>20</sub> H <sub>19</sub> O <sub>4</sub> N <sub>2</sub>	Equivalent 337	Equivalent 338
10.	2-Methoxy-5-methyl-phenyl-	M. P. 98	C <sub>14</sub> H <sub>12</sub> O <sub>4</sub>	C=67.5, H=6.4	C=67.7; H=6.5%
11.	Semicarbazone of (9)	M. P. 152	C <sub>15</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub>	Equivalent 303	Equivalent 305
12.	Phenylhydrazone of (9)	M. P. 122			
13.	Phenyl-	M. P. 109	C <sub>15</sub> H <sub>12</sub> O <sub>3</sub>	C=70.5, H=5.7	C=70.6, H=5.9%
14.	Semicarbazone of (11)	M. P. 152	C <sub>15</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub>	Equivalent 259	Equivalent 261
	Phenyl hydrazone of (11)	M. P. 145	C <sub>15</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub>	Equivalent 292	Equivalent 294
15.	<i>β</i> -Aryl-T-aceto-butyric-acids				
16.	4-Methoxy-3-methyl-phenyl-	M. P. 72	C <sub>14</sub> H <sub>12</sub> O <sub>4</sub>	C=67.1; H=7.0	C=67.2, H=7.2%
17.	Semicarbazone of (15)	M. P. 178	C <sub>15</sub> H <sub>13</sub> O <sub>4</sub> N <sub>3</sub>	Equivalent 308	Equivalent 307
18.	2-Methoxy-5-methyl-phenyl-	M. P. 98	C <sub>14</sub> H <sub>12</sub> O <sub>4</sub>	C=67.0; H=7.1	C=67.2, H=7.2%
19.	Semicarbazone of (17)	M. P. 199			
	Phenyl-	M. P. 85			
	(Cf. Vorländer, Annalen 1896, 294, 253)				

		M. P. 175	$C_{13}H_{17}O_3N_3$	Equivalent 261	Equivalent 263
20.	Semicarbazone of (19)				
21.	R- <i>a</i> -methyl-benzylidene-acetones 4-Methoxy-3-methyl-	B. P. 145-150 5 mm.	$C_{13}H_{14}O_3$	C = 76.4; H = 7.8	C = 76.5, H = 7.9 %
22.	Semicarbazone of (21)	M. P. 205	$C_{14}H_{19}O_3N_3$	C = 64.2; H = 7.1	C = 64.4; H = 7.3 %
23.	Oxime of (21)	M. P. 100	$C_{13}H_{17}O_3N$	C = 71.2; H = 6.8	C = 71.2; H = 6.9 %
24.	2-Methoxy-5-methyl-	B. P. 135 5 mm.	$C_{13}H_{18}O_3$	C = 76.3; H = 7.7	C = 76.5, H = 7.9 %
25.	Semicarbazone of (24)	M. P. 200			
26.	R = H	B. P. 125 5 mm.	$C_{11}H_{13}O$	C = 65.3; H = 7.5	C = 65.4; H = 7.5 %
27.	Semicarbazone of (26)	M. P. 190			
28.	$\beta$ -Aryl-methylene glutaconides				
29.	4-Methoxy-3-methyl-phenyl- Phenyl-	M. P. 95 M. P. 96	$C_{14}H_{14}O_3$ $C_{13}H_{13}O_3$	C = 73.9; H = 5.8 C = 77.2; H = 5.3	C = 74.0, H = 6.1 % C = 77.4; H = 5.4 %
30.	4-Methoxy-3-methyl- $\beta$ -methyl- cinnamic acid	M. P. 145	$C_{13}H_{14}O_3$	Equivalent 206	Equivalent 206

## INHIBITIVE POWER OF GELATINE

By

B N DESAI and B M. NAIK.

Bolam and Desai (Trans. Faraday Soc., 24, 50, 1928) have observed that the time required for the appearance of red coloured precipitate from a yellow mixture of  $\text{AgNO}_3$  and  $\text{K}_2\text{CrO}_4$  in gelatine decreases and its  $p_H$  increases on subjecting it to hydrolysis. This property of preventing the precipitation of insoluble salt has been termed "inhibitive power". Desai and Nabar (Journ. University of Bombay 1, Part II, 28, 1932) have shown that the inhibitive power of gelatine with reference to  $\text{Ag}_2\text{CrO}_4$  increases on decreasing the  $p_H$  of gelatine. Desai and Nabar (Trans. Faraday Soc. 28, 449, 1932; also see Bolam and Mackenzie, *ibid*, 22, 151, 162, 1926) have further shown that in the yellow coloured mixture  $\text{Ag}_2\text{CrO}_4$  exists in ionic condition. In the present paper are given the results of the study of precipitation of  $\text{Ag}_2\text{CrO}_4$ ,  $\text{AgI}$  and  $\text{PbI}_2$  in gelatine under different conditions.

(a) *Preparation of  $\text{Ag}_2\text{CrO}_4$  in samples of gelatine of different  $p_H$*

The gelatine used in these experiments contained 1.177% ash and 18% moisture. The inhibitive power was determined in exactly the same manner as before. The  $p_H$  of gelatine was determined colourometrically. Samples of gelatine having different  $p_H$  were prepared by adding suitable amounts of acetic acid or sodium acetate. Experiments were carried out by using different equivalent amounts of the reactants. The results of these experiments are given in Tables I to VII.

TABLE I.  
Total Volume of mixture = 20 c. c.  
Concentration of gelatine = 3%.

$P_g$  of gelatine = 4.5.

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

5 c. c. $\frac{N}{100} AgNO_3 +$ 5 c. c. $\frac{N}{100} K_2CrO_4$		6 c. c. of $\frac{N}{100} AgNO_3 +$ 6 c. c. $\frac{N}{100} K_2CrO_4$		7 c. c. $\frac{N}{100} AgNO_3 +$ 7 c. c. $\frac{N}{100} K_2CrO_4$		8 c. c. $\frac{N}{100} AgNO_3 +$ 8 c. c. $\frac{N}{100} K_2CrO_4$		9 c. c. $\frac{N}{100} AgNO_3 +$ 9 c. c. $\frac{N}{100} K_2CrO_4$	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
0.6	1	1.0	2	1.4	2	1.9	2	2.4	2
0.7	2	1.1	6	1.5	4	2.0	4	2.6	5
0.8	7	1.2	16	1.6	9	2.1	7	2.8	11
0.9	19	1.3	45	1.7	24	2.2	13	3.0	21
1.0	43	1.4	120	1.8	49 to 50	2.3	23	3.2	40
						2.4	44		

TABLE II.

Total volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

pH of gelatine = 4.75.

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

4 c. c. $\frac{N}{100}$ AgNO <sub>3</sub> + 4 c. c. $\frac{N}{100}$ K <sub>2</sub> CrO <sub>4</sub>		5 c. c. $\frac{NO}{100}$ AgNO <sub>3</sub> + 5 c. c. $\frac{N}{100}$ K <sub>2</sub> CrO <sub>4</sub>		6 c. c. $\frac{N}{100}$ AgNO <sub>3</sub> + 6 c. c. $\frac{N}{100}$ K <sub>2</sub> CrO <sub>4</sub>		7 c. c. $\frac{N}{100}$ AgNO <sub>3</sub> + 7 c. c. $\frac{N}{100}$ K <sub>2</sub> CrO <sub>4</sub>	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1.0	1	1.8	1	2.8	1	4.0	2
1.2	3	1.9	2	3.0	3	4.2	3
1.4	10	2.0	3	3.2	6	4.4	5
1.6	24	2.1	6	3.4	13	4.6	9
1.8	50 to 51	2.2	9	3.6	26	4.8	15
		2.3	13	3.8	53	5.0	25
		2.4	21			5.2	39
		2.5	30				

TABLE III.

Total volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

pH of gelatine = 5.00.

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

4 c. c. $\frac{N}{100}$ $AgNO_3 +$ 4 c. c. $\frac{N}{100}$ $K_2CrO_4$	5 c. c. $\frac{N}{100}$ $AgNO_3 +$ 5 c. c. $\frac{N}{100}$ $K_2CrO_4$		6 c. c. $\frac{N}{100}$ $AgNO_3 +$ 6 c. c. $\frac{N}{100}$ $K_2CrO_4$		7 c. c. $\frac{N}{100}$ $AgNO_3 +$ 7 c. c. $\frac{N}{100}$ $K_2CrO_4$	
	(1)	(2)	(1)	(2)	(1)	(2)
1.6	2	2.8	1	4.2	5.8	1
1.8	4	3.0	2	4.4	6.1	2
2.0	8	3.2	4	4.6	6.4	4
2.2	13	3.4	6	4.8	6.7	6
2.4	23	3.6	11	5.0	7.0	10
2.6	35	3.8	17	5.2	7.3	16
		4.0	27	5.4	7.6	25
		4.2	42	5.6	7.9	39
				5.8		



TABLE IV.

Total volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

pH of gelatine = 5.25.

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

	4 c. c. $\frac{N}{100}$ AgNO <sub>3</sub> + 4 c. c. $\frac{N}{100}$ K <sub>2</sub> CrO <sub>4</sub>		5 c. c. $\frac{N}{100}$ AgNO <sub>3</sub> + 5 c. c. $\frac{N}{100}$ K <sub>2</sub> CrO <sub>4</sub>		6 c. c. $\frac{N}{100}$ AgNO <sub>3</sub> + 6 c. c. $\frac{N}{100}$ K <sub>2</sub> CrO <sub>4</sub>		7 c. c. $\frac{N}{100}$ AgNO <sub>3</sub> + 7 c. c. $\frac{N}{100}$ K <sub>2</sub> CrO <sub>4</sub>	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1.7		1	3.7	4	5.2	3	7.0	2
2.0		4	4.0	8	5.6	6	7.4	4
2.3		10	4.3	14	6.0	10	7.8	7
2.6		20	4.6	23	6.4	19	8.2	10
2.9		37	4.9	40	6.8	33	8.6	17
3.1		53	5.2	63	7.2	54	9.0	27
					7.6	85 to 87	9.4	43

TABLE V.

Total volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

pH of gelatine = 5.52 (gelatine as such).

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

4 c. c. $\frac{N}{100}$ $AgNO_3 +$ 4 c. c. $\frac{N}{100}$ $K_2CrO_4$	(1)		(2)		5 c. c. $\frac{N}{100}$ $AgNO_3 +$ 5 c. c. $\frac{N}{100}$ $K_2CrO_4$		6 c. c. $\frac{N}{100}$ $AgNO_3 +$ 6 c. c. $\frac{N}{100}$ $K_2CrO_4$		7 c. c. $\frac{N}{100}$ $AgNO_3 +$ 7 c. c. $\frac{N}{100}$ $K_2CrO_4$	
	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
1.6		1	3.4	1	5.4	2	7.4	2		
1.9		3	3.7	3	5.7	3	7.7	3		
2.2		6	4.0	5	6.0	6	8.0	5		
2.5		12	4.3	8	6.3	9	8.3	8		
2.8		23	4.6	15	6.6	13	8.6	11		
3.1		41	4.9	25	6.9	20	8.9	17		
			5.2	39	7.2	27	9.3	26		
							9.7	42		

TABLE VI.

Total Volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

pH of gelatine = 5.75.

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

4 c. c. $\frac{N}{100}$ $AgNO_3 +$ 4 c. c. $\frac{N}{100}$ $K_2CrO_4$		5 c. c. $\frac{N}{100}$ $AgNO_3 +$ 5 c. c. $\frac{N}{100}$ $K_2CrO_4$		6 c. c. $\frac{N}{100}$ $AgNO_3 +$ 6 c. c. $\frac{N}{100}$ $K_2CrO_4$		7 c. c. $\frac{N}{100}$ $AgNO_3 +$ 7 c. c. $\frac{N}{100}$ $K_2CrO_4$	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
2.4	3	4.4	2	6.5	2	9.4	2
2.7	5	4.7	3	6.8	3	9.8	3
3.0	10	5.0	5	7.1	3	10.2	3
3.3	17	5.3	7	7.4	4	10.6	4
3.6	31	5.6	10	7.7	5	11.0	6
3.9	48	5.9	15	8.0	6	11.4	8
		6.2	21	8.3	8	11.8	10
		6.5	29	9.0	15	12.2	13
						12.6	17
						13.0	21

TABLE VII.

Total volume of mixture = 20 c. c.

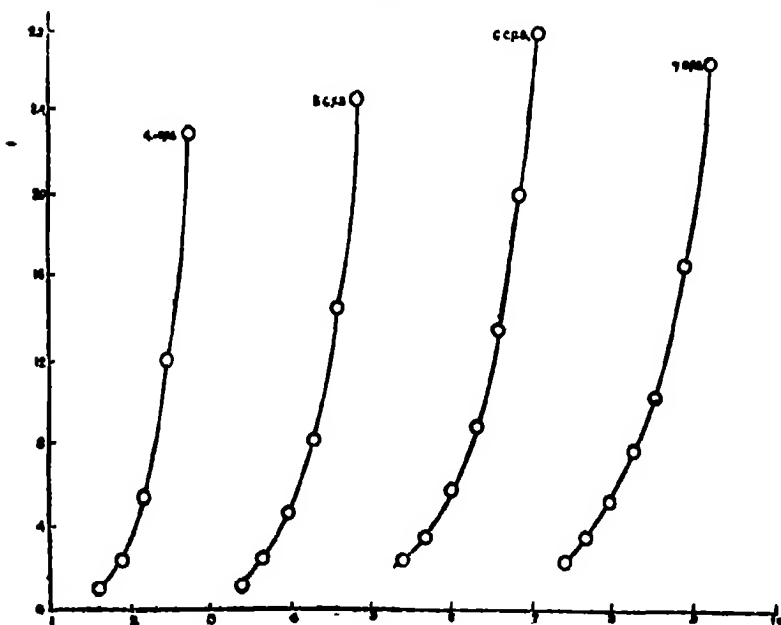
Concentration of gelatine = 3%.

 $p_H$  of gelatine = 6.00.

5 c. c. of $\frac{N}{100}$ $AgNO_3$ + 5 c. c. of $\frac{N}{100}$ $K_2CrO_4$	
c. c. of gelatine.	Time of Inhibition in minutes.
3.8	2
4.1	4
4.4	7
4.7	13
5.0	20

It will appear from the tables that in every case the time of inhibition or the inhibitive power of gelatine increases with an increase in the amount of gelatine added. In Fig 1 is plotted the amount of

FIG. 1.

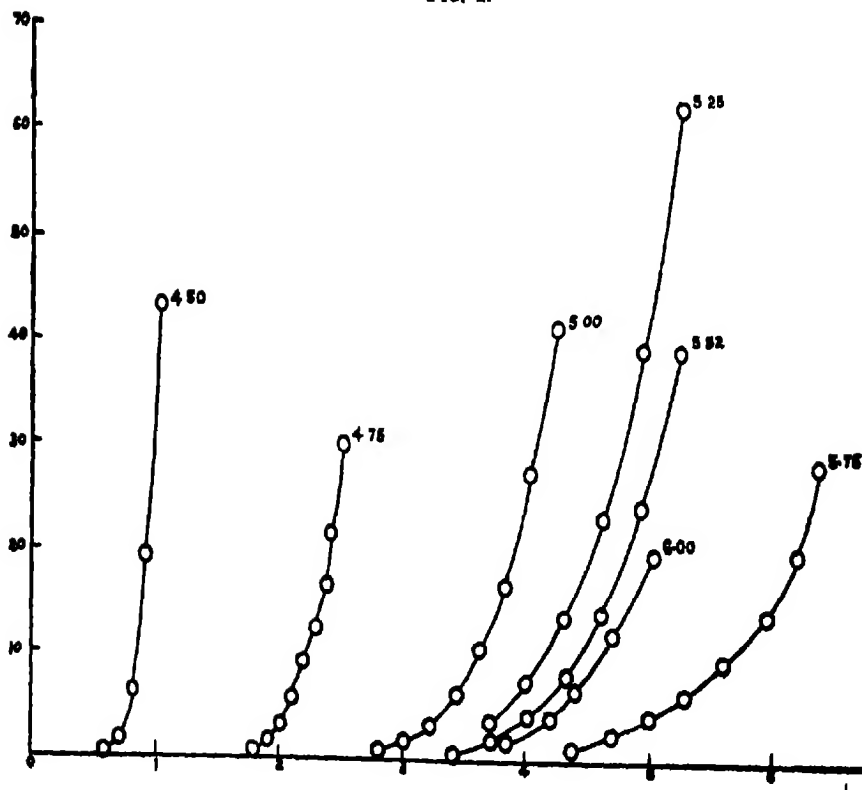


gelatine solution against the time of inhibition for different equivalent amounts of reactants in gelatine having  $p_H$  5.52. It will be seen from the figure that as the amount of the reactants decreases the curve is

displaced more and more towards the Y-axis and that the curves are displaced by almost the same distance for a change in the amount of the reactants by 1 c. c. It would thus appear as if the amount of the reactants whose curve corresponds to the ordinate will approximately give an idea about the solubility of  $\text{Ag}_2\text{CrO}_4$  in that particular sample of gelatine. The curves for other samples of gelatine are also exactly of the same nature as those given in Fig. 1. The solubility of  $\text{Ag}_2\text{CrO}_4$  in gelatine of  $p_H$  5.75 calculated on the basis of above ideas comes to about 10 times more than that in water. The solubility of  $\text{Ag}_2\text{CrO}_4$  in samples of  $p_H$  4.5 and 6.0 comes to about 10% more than that in gelatine of  $p_H$  5.75. It would thus appear that although with slight changes in the  $p_H$  of gelatine the inhibitive power changes considerably, the solubility of  $\text{Ag}_2\text{CrO}_4$  in gelatine is not affected to any appreciable extent by those changes. These results are therefore in line with those obtained by Desai and Nabar (Journ. University of Bombay, loc. cit.).

In Fig. 2 is plotted the amount of gelatine (C) against the time of

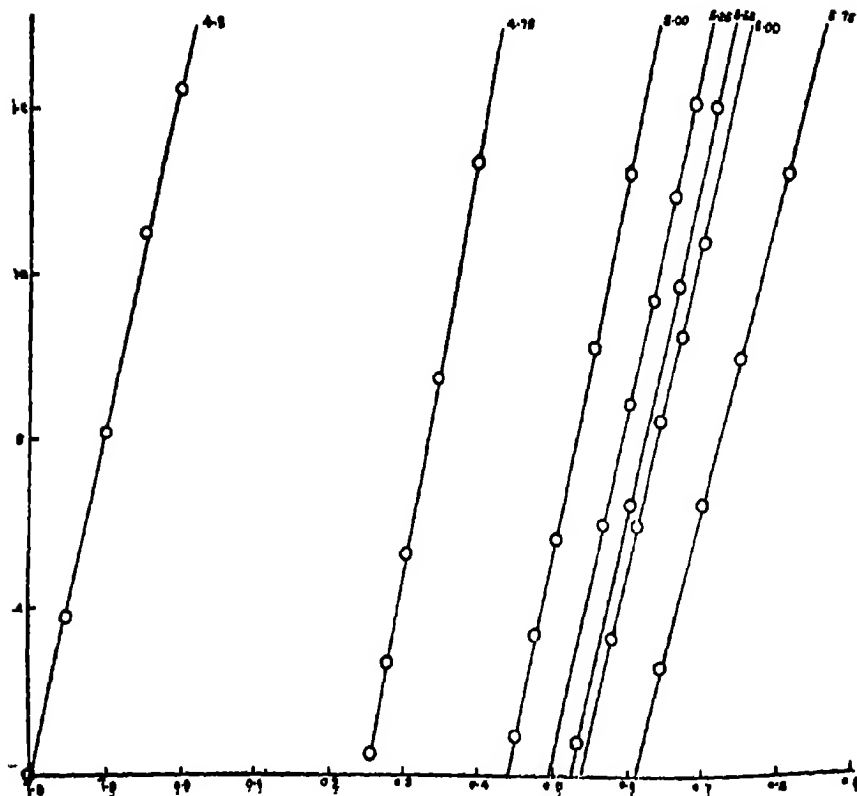
FIG. 2.



inhibition (T) for samples of different  $p_H$  in the case of 5 c. c. of  $\frac{N}{100} \text{AgNO}_3 + 5 \text{ c. c. of } \frac{N}{100} \text{K}_2\text{CrO}_4$ . It will appear from the figure that the curves for samples of gelatine of  $p_H$  either smaller or larger than 5.75 are displaced towards the left of the curve for  $p_H$  5.75. Also as the  $p_H$  increases or decreases more and more than 5.75 the curves are displaced more and more towards the ordinate. The curves obtained with different amounts of the reactants show exactly the same behaviour. These results thus show that the inhibitive power of gelatine of  $p_H$  5.75 is minimum and that the inhibitive power of other samples of gelatine of  $p_H$  smaller or larger than 5.75 is greater than that of sample of  $p_H$  5.75. These results have a very important bearing on the nature of rings of  $\text{Ag}_2\text{CrO}_4$  in gelatine for as argued by Desai and Nabar (Journ Indian Chem Soc., 9, 141, 1932) there might be a definite range of  $p_H$  of gelatine within which good rings can be obtained. This point will however be dealt with in another paper.

In Fig. 3 is given the plot of  $\log C$  and  $\log T$  for the same values

FIG. 3



which have been used in Fig. 2. It will appear from this figure that the plot is a straight line and the relation between  $C$  and  $T$  can be expressed by an equation of the form

$$T = K (C)^m$$

where  $K$  and  $m$  are constants. The time of inhibition thus varies exponentially with the amount of gelatine.

In Table VIII are given the results of inhibitive power of gelatine with reference to  $Ag_2CrO_4$  obtained in another manner. In these experiments the amount of  $Ag_2CrO_4$  that can be kept in the mixture for 10 minutes before the appearance of the red colour when 6 c. c. of 3% gelatine solution are added, has been determined.

TABLE VIII.

Total volume of the mixture = 20 c. c.

Concentration of gelatine = 3%.

Amount of gelatine = 6 c. c. in 20 c. c. of mixture.

Time of inhibition (fixed) = 10 minutes.

$p_H$ of gelatine	c. c. of $\frac{N}{100} Ag_2CrO_4$
4.25	22.0
4.50	12.0
4.75	8.6
5.00	6.8
5.25	6.1
5.52	5.7
5.75	5.3
6.00	5.6
6.25	6.4

It will appear from the results given in the above table that here also gelatine of  $p_H$  5.75 has got the smallest inhibitive power, while samples of gelatine having  $p_H$  smaller or larger than 5.75 show greater inhibitive power.

*I (b) Changes in Inhibitive Power and Gold Number of Gelatine Hydrolysed to Different Extents*

The hydrolysis of gelatine was carried out by boiling a 3% solution in a silica flask in a paraffin bath whose temperature was maintained at  $115^\circ C$ . Any loss in weight due to heating, which was always small, was made good by adding distilled water. The inhibitive power was determined by finding out the amount of  $Ag_2CrO_4$  that can be kept in solution state (i.e., till the red coloured precipitate appears) for 10 minutes, the volume of the mixture being kept constant throughout. The gold numbers were determined in the usual manner. The results of these experiments are given in Table IX,

TABLE IX.

Total volume of mixture (for inhibitive power) = 20 c. c.  
 Conc. of gelatine = 3%.  
 Conc. of gelatine (for protective power) = 0.001%.  
 Time of inhibition = 10 minutes.

Gelatine hydrolysed for hours.	Resulting $p_H$	c. c. of $\frac{N}{100}$ $Ag_2CrO_4$ .	Gold Numbers.
0 (dispersed at 40°C.)	5.52	5.67	0125
1	5.54	5.60	0139
2	5.57	5.55	0149
4	5.62	5.50	0160
7	5.69	5.40	0168
10	5.72	5.35	0172

It will appear from the table that on hydrolysing the gelatine its  $p_H$  increases. This is in agreement with what has been observed by Bolam and Desai (loc. cit.) and by Desai and Nabar (Trans. Faraday Soc., loc. cit.). Also hydrolysed gelatine is found to be less effective in preventing precipitation than unhydrolysed gelatine. Bolam and Desai (loc. cit.) got a clear indication of a maximum in the value of time of inhibition (inhibitive power) at a certain stage of hydrolysis. Such a maximum in the inhibitive power has not been observed in the present case, probably due to the fact that hydrolysis has been carried out at a higher temperature.

The gold numbers increase on hydrolysing gelatine. If the gold numbers are taken to indicate the protective power of gelatine as is usually done, the results show that the protective power of gelatine decreases with an increase in the degree of hydrolysis. Ganguly (Journ. Indian Chem. Soc., 3, 177, 1926) observed that on hydrolysing gelatine the gold numbers first decrease and then increase. In view of the fact that gelatine solution has been boiled freely in silica flask in Ganguly's as well as our experiments it is not understood why a minimum in the value of gold numbers has not been observed in the present case.

In order to see how far the changes in the inhibitive and protective power of gelatine on hydrolysis are brought about by a change in the acidity of gelatine, some experiments were also carried out by bringing back the  $p_H$  of hydrolysed gelatine to original value and then determine its inhibitive power and gold numbers. These results are given in Table X.



TABLE X.

Inhibitive and protective power on restoring  $p_H$  to original value.

Gelatine hydrolysed for hours.	$p_H$ of hydrolysed gelatine brought back to the value	c. c. of $\frac{N}{100}$ $Ag_2CrO_4$ .	Gold Numbers.
1	5.52	5.66	.0126
2	5.51	5.67	.0128
4	5.50	5.66	.0128
7	5.52	5.67	.0128
10	5.50	5.67	.0130

It will appear from the above table that on restoring the  $p_H$  of hydrolysed gelatine to its original value (i. e., to the value of  $p_H$  of unhydrolysed gelatine) both the inhibitive power as well as gold numbers become the same as for unhydrolysed gelatine. These results thus show that changes in inhibitive and protective power brought about by hydrolysis are mainly due to a change in acidity of gelatine.

Bolam and Desai (loc. cit.) have stated that obviously inhibition and protection do not go hand in hand for there is a difference in the function of gelatine in the two cases. In the former rôle gelatine opposes the formation or growth of crystallisation centres and thus gives rise to a highly supersaturated solution, in the latter rôle gelatine prevents aggregation of small particles to larger masses and thus gives rise to a colloidal solution. On comparing the results of inhibition and gold numbers on hydrolysis it will appear that if gold numbers are taken to indicate the protective power, both inhibitive and protective power of gelatine decrease on hydrolysis. This is apparently not in agreement with the view of Bolam and Desai. Hydrolysis increases the degree of dispersion of the precipitate as has been observed by Bolam and Desai (loc. cit.) as well as in these experiments. This is due to the fact that there is less resistance to the growth of crystallisation centres in the former case (less inhibitive power) and therefore if the number of crystallisation centres is large, one would naturally expect that, other things remaining same, the particles of the precipitate will be smaller in hydrolysed than in unhydrolysed gelatine. The changes in the gold numbers on hydrolysis can be due to either changes in the protective power as seen from finer precipitate or changes in the acidity of gelatine which affect coagulation of gold sol. The original gold number having been obtained on restoring the original  $p_H$ , it appears that the gold number changes on hydrolysis are mostly due to the effect of changes of acidity on the coagulation of gold sol,

In Table XI are given the values of gold numbers for samples of unhydrolysed gelatine of different  $p_H$ .

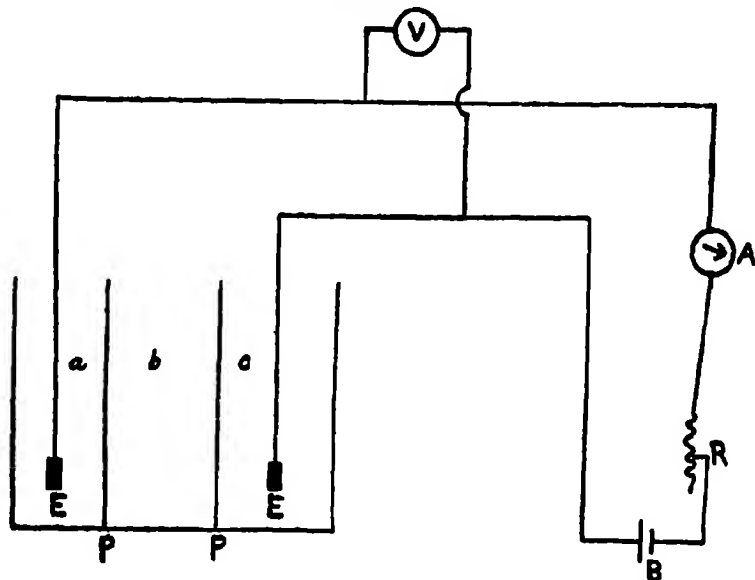
TABLE XI.

$p_H$ of gelatine made equal to that of hydrolysed gelatine.	Gold Numbers.
5.57	.0139
5.62	.0160
5.69	.0165
5.72	.0172

It will appear from the results that with a decrease in the acidity of gelatine the gold number increases. Also whether the changes in  $p_H$  are brought about by hydrolysis (Table IX) or by adding sodium acetate (Table XI) the gold numbers change in the same fashion and almost to the same extent for same changes in  $p_H$ .

The changes in the inhibitive power of gelatine on hydrolysis would also seem to be wholly due to changes in its acidity as shown by results given in Tables VIII, IX and X. These results thus show that changes in the inhibitive power and gold numbers on hydrolysis are due to changes in its  $p_H$ .

DIA. A.



duced light. On mixing solutions of  $\text{AgNO}_3$  in gelatine, and  $\text{KI}$  in gelatine, the mixture attained somewhat greenish colour although no precipitation was visible. When precipitate of  $\text{AgI}$  began to separate from the mixture the colour changed to whitish yellow. The time required to get the whitish yellow colour of the same intensity as the standard was taken as a measure of inhibitive power in each case. The results of these experiments are given in Table XV.

TABLE XV.

Total volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

3 c c of  $\frac{N}{10}$   $\text{KI}$  + 3 c. c. of  $\frac{N}{10}$   $\text{AgNO}_3$

Column (1) c. c. of gelatine and column (2) Time of inhibition in minutes.

$p_H = 4.5$		$p_H = 4.75$		$p_H = 5.00$		$p_H = 5.25$	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
6.4	8	5.8	8	5.4	8	5.2	8
8.0	16	7.3	16	6.8	16	6.6	16
9.2	24	8.4	24	7.8	24	7.6	24
10.0	32	9.2	32	8.6	32	8.3	32

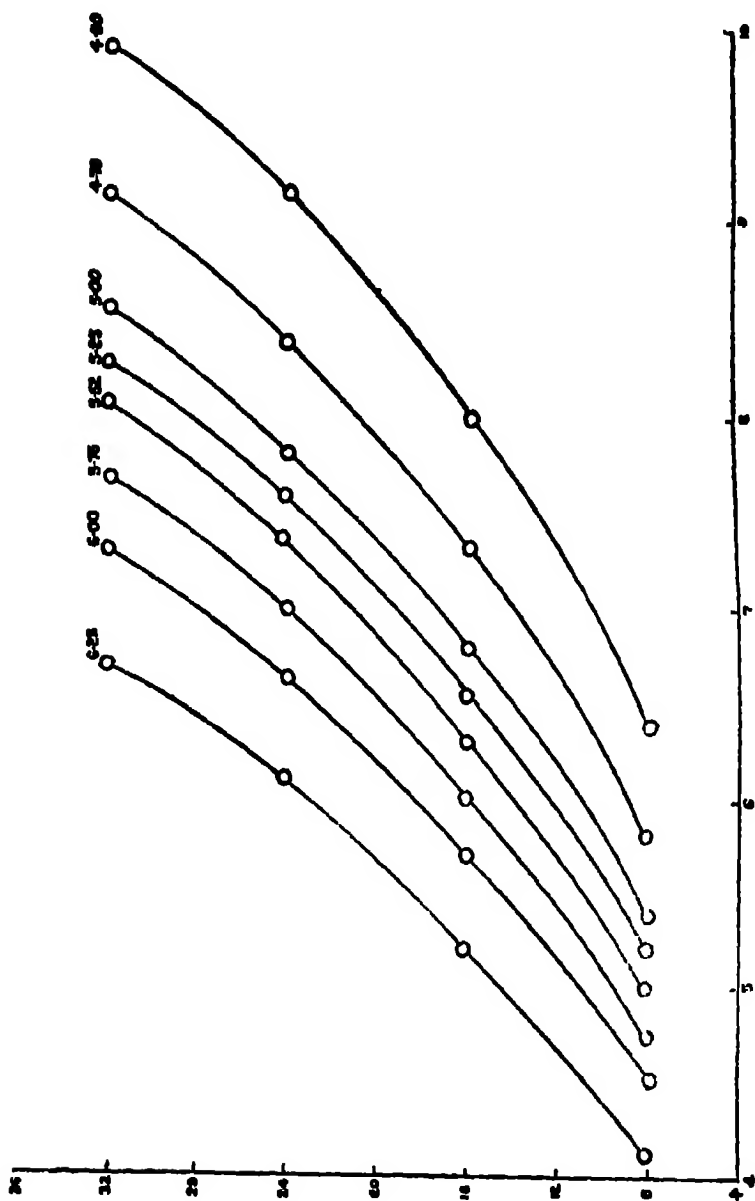
  

$p_H = 5.52$		$p_H = 5.75$		$p_H = 6.00$		$p_H = 6.25$	
(1)	(2)	(1)	(2)	(1)	(2)	(1)	(2)
5.0	8	4.7	8	4.5	8	4.1	8
6.3	16	6.0	16	5.7	16	5.2	16
7.4	24	7.0	24	6.6	24	6.1	24
8.1	32	7.7	32	7.3	32	6.7	32

It will be seen from the above table that for all samples of gelatine the inhibitive power increases with an increase in amount of gelatine. This has also been observed in the case of  $\text{Ag}_2\text{CrO}_4$ . In Fig. 4 is given the plot of the amount of gelatine added (C) and the time of inhibition (T) for different samples of gelatine. It will appear from the figure that as the  $p_H$  of gelatine decreases the curves are displaced more and more away from the ordinate. In other words the inhibitive power decreases with a decrease of  $p_H$  of gelatine solution. This behaviour is therefore quite different from that with  $\text{Ag}_2\text{CrO}_4$ . This difference in the inhibitive power in the two cases probably influences the nature of rings of  $\text{AgI}$

and  $\text{Ag}_2\text{CrO}_4$  in gelatine. We have observed that the nature of  $\text{AgI}$  and  $\text{Ag}_2\text{CrO}_4$  rings in gelatine is not similar. This point will be dealt with separately elsewhere.

FIG. 4



In this case also as with  $\text{Ag}_2\text{CrO}_4$  the plot of  $\log C$  and  $\log T$  is a

straight line. The inhibitive power thus varies exponentially with the amount of gelatine.

### III. Precipitation of $PbI_2$ in samples of Gelatine of different $p_H$ .

When  $Pb(NO_3)_2$  in gelatine and KI in gelatine are mixed, the mixture is clear and colourless. However on allowing the mixture to stand the colour becomes greenish in the beginning and yellow later on. The greenish coloured mixture did not contain any particles of  $PbI_2$  and was clear, while the yellow coloured mixture was opaque. The time required to get both greenish and yellow colour of the same intensity as the standards was taken as a measure of inhibitive power in each case. The results are given in Table XVI.

TABLE XVI.

Total volume of mixture = 20 c. c.

Concentration of gelatine = 3%.

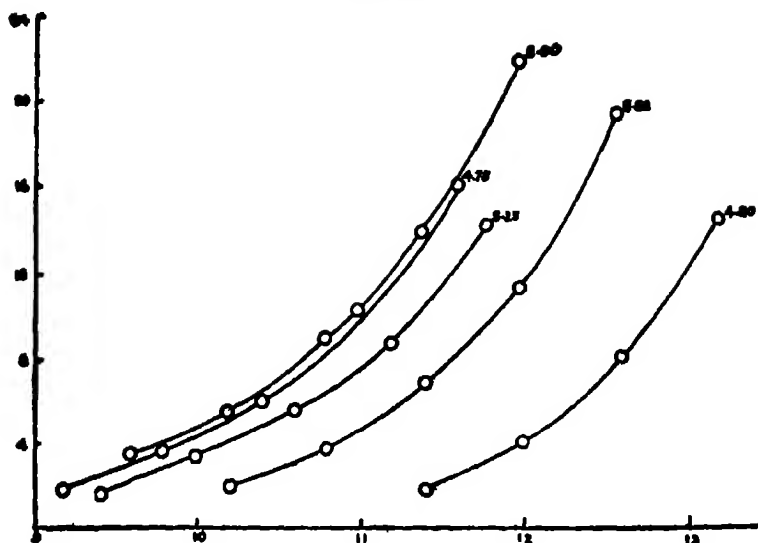
$$2.5 \text{ c. c. of } \frac{N}{10} \text{ KI} + 2.5 \text{ c. c. of } \frac{N}{10} \text{ Pb(NO}_3)_2.$$

Column (1) c. c. of gelatine and columns (2) and (3) Time of inhibition in minutes for appearance of greenish and yellow colour respectively.

$p_H=5.52$			$p_H=5.25$			$p_H=5.00$			$p_H=4.75$			$p_H=4.5$		
(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)	(1)	(2)	(3)
10.2	2	3	9.4	2	3	9.6	3	6	8.6	—	2	11.4	2	3
10.8	3	7	10.0	3	6	10.2	5	10	9.2	2	4	12.0	3	7
11.4	7	11	10.6	5	9	10.8	9	15	9.8	3	7	12.6	7	13
12.0	11	19	11.2	8	15	11.4	13	25	10.4	6	12	13.2	14	25
12.6	19	35	11.8	14	24	12.0	21	37	11.0	10	20			
									11.6	16	33			

It will appear from the table that, as in the case of  $Ag_2CrO_4$  and  $AgI$ , here also the inhibitive power increases with an increase in the amount of gelatine added. In Fig. 5 is plotted the amount of gelatine (C) against the time of inhibition (T) in different cases. It will be seen from the figure that the curves for  $p_H$  greater or smaller than 5.0 are displaced towards the right of the curve for  $p_H$  5.0. In other words the inhibitive power of gelatine with reference to  $PbI_2$  is maximum for  $p_H$  5.0 and smaller for higher or lower values of  $p_H$ . This behaviour of inhibitive power might have an important bearing on the nature of  $PbI_2$  rings in gelatine. The  $PbI_2$  rings in samples of gelatine of different  $p_H$  are under investigation.

FIG. 5.



## SUMMARY.

Inhibitive power of samples of gelatine of different  $p_H$  with reference to precipitation of  $Ag_2CrO_4$ ,  $AgI$  and  $PbI_2$ , has been determined. In all the cases the inhibitive power increases with an increase in the amount of gelatine added and the plot of  $\log C$  (amount of gelatine added) and  $\log T$  (time of inhibition) is a straight line. It is found that the inhibitive power with reference to  $Ag_2CrO_4$  is minimum for gelatine of  $p_H$  5.75 and is greater for higher or lower values of  $p_H$ . In the case of  $AgI$  the inhibitive power continuously decreases with a decrease of  $p_H$  of gelatine. The inhibitive power with reference to  $PbI_2$  is maximum for gelatine of  $p_H$  5.0 and is smaller for higher or lower values of  $p_H$ . It is suggested that the difference in the inhibitive power with reference to  $Ag_2CrO_4$ ,  $AgI$  and  $PbI_2$  might have an important bearing on the nature of rings of these substances in gelatine.

On hydrolysing gelatine, its  $p_H$  and gold number increase while inhibitive power with reference to  $Ag_2CrO_4$  decreases. When gelatine solution is electrodialysed, its  $p_H$  and gold number decrease while inhibitive power with reference to  $Ag_2CrO_4$  increases. On bringing back the  $p_H$  of gelatine to its original value both the original inhibitive power and gold numbers are restored, thus showing that the changes are mainly due to changes in  $p_H$  of gelatine. It is observed that the products of hydrolysis have less protective power than products of electrodialysis.

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Bombay.

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*Note*—Since the present paper was submitted for publication there has appeared a paper by Bolam and Donaldson (Trans. Faraday Soc., 29, 864, 1933) on the influence of gelatine on precipitation of silver chromate. From Fig 1 of their paper it is clear that the inhibitive power (property of preventing the precipitation of insoluble salt) of gelatine steadily increases with an increase of acidity of gelatine ( $p_H$  range tried by them is 5.7 to 4.3). Our results (Fig. 2 of our paper) also point to the same conclusion for the same range of  $p_H$  and their results thus completely support our results. On p. 876 of their paper Bolam and Donaldson have calculated the degree of supersaturation according to the theory of Von Weimarn (Kolloid—Z, 2, 199, 1908, etc.; 3, 3, 1908, etc., 4, 27, 1909, Grundzüge der Dispersoidchemie, 1911; Zum Lehre von dem Zustanden der Materie, 1914) and found that the degree of supersaturation increases slightly as the  $p_H$  decreases from 5.7 to 5.0, and then falls off more rapidly as the  $p_H$  is further decreased. They conclude that the degree of supersaturation, and therefore the inhibitive action of the gelatine, probably has an optimum value at  $p_H=5.0$ . It is difficult to reconcile this latter conclusion with the inferences that can be drawn from Fig. 1 of their paper as well as with our present results. It may however be pointed out that the optimum value of supersaturation for gelatine of  $p_H=5.0$  seems to influence considerably the nature and number of  $Ag_2CrO_4$  rings in gelatine, for as our results have shown (will be published in due course) best rings are obtained in samples of gelatine of  $p_H$  range 5.0 to 5.25.

# THE ACTION OF NITRIC ACID ON TIN

By

G. S. KASBEKAR and A. R. NORMAND

## *Introduction.*

The reaction between nitric acid and metals has been studied by many workers, but as it is very complex no general conclusion has yet been reached. At the end of this reaction there are generally present not only the nitrate and nitrite, but also a large number of reduction products of the acid. Ackworth and Armstrong (Jour. Chem. Soc. 32, 54, 1877) suggested that the nitrate was formed first, along with nascent hydrogen, which would reduce the excess nitric acid. Divers attempted to explain the formation of ammonia during the reduction (Jour. Chem. Soc. 43, 465, 1883) and Veley (Proc. Roy. Soc. 46, 216, 1890) attributed the inception of the reaction to the presence of nitrous acid. Gmelin (Hand book of Chem. London, 359, 397, 1849) supposed that the metals are first oxidised, the oxide then dissolving in the acid to yield the nitrate. If the metal decomposes water there would also be products such as ammonia, hydroxylamine, etc. Bancroft (Jour. Phys. Chem. 28, 475, 1924) considers the reaction as a case of electrolytic corrosion, and points out that the hypothesis of Ackworth and Armstrong is a special case of this. On the same basis Milligan (Jour. Phys. Chem. 28, 744, 1924) and Joss (Jour. Phys. Chem. 1222, 30, 1926) have presented a systematic scheme representing the stages in which the reduction of nitric acid proceeds, but this scheme has not yet been proved to be applicable when the reduction is due to metals.

The literature shows that no worker has made a complete study of the reaction between a metal and nitric acid. In the case of tin Ackworth and Armstrong studied the gaseous products, whereas Walker and Veley (Jour. Chem. Soc. Trans. 846, 1893) studied the conditions in which tin goes into solution. It appeared to us that a systematic analysis of all the products formed in the mixture during the reaction between a metal and nitric acid, under varying conditions, would lead to definite conclusions about their stability and their causes of formation. Tin was chosen for a complete study on account of its amphoteric nature, its multivalent behaviour, and the instability of its compounds.

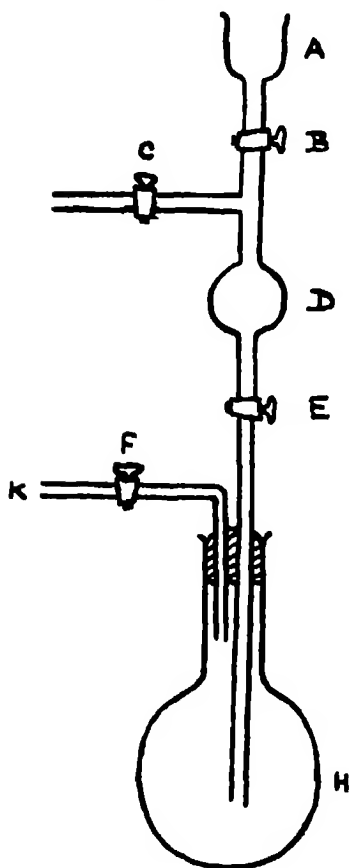
## *Experimental.*

For the study of the products in solution, the following procedure was adopted. A known amount of the acid, of a definite concentration,



was introduced into a graduated 250 c. c. flask, kept in a water thermostat. The air was displaced by bubbling carbon dioxide through the acid for a long time. Small pieces of tin foil were introduced, and the time was measured for it to dissolve completely. Then the contents of the flask were diluted to 250 c. c. and the mixture was analysed qualitatively and quantitatively. The stannous tin was estimated by the iodine method of Lenssen as modified by Hallet (*Jour. Soc. Chem*

FIG. 1.



H was then evacuated through F. By opening E, acid could then be introduced into H, and the evolved gases collected through F. A Sprengel pump was used to evacuate the system and collect the gases.

For the estimation of the gaseous products, Milligan's method (*Jour. Phys. Chem.* 28, 544, 1924) was followed in detail. Nitrogen peroxide was estimated by absorption in concentrated sulphuric acid, and nitric oxide by absorption in a mixture of concentrated sulphuric acid and nitric acid in the proportion 50 : 1 by volume. The remaining

*Indus.* 35, 1087, 1916). The stannic tin was determined as the difference between the stannous and total tin. The total tin was estimated by weighing it as stannic oxide. Kjeldahl's method was used for the estimation of ammonia, with due precautions on account of the presence of other substances. Hydroxylamine was estimated by converting it to ammonia by the use of titanium chloride. The nitrates were estimated by the oxidation of ferrous chloride. All the above methods were tested beforehand and were found to be sufficiently accurate for the purposes of this investigation.

For the study of the gaseous products the apparatus shown in Fig. 1 was used. The tin was first introduced into the flask H and the stopper closed. With E closed, and B and C open, nitric acid was introduced through A into D. B was then closed, and the space above the acid in D was evacuated through C. The flask

TABLE I.  
Reaction between nitric acid and tin. (Varying concentration of nitric acid).

Experiment No.	HNO <sub>3</sub> conc. g/c.c.	Acid c.c.	Tin grams.	Temperature °C.	Time minutes.	Sn gms.	Sn gms.	NH <sub>3</sub> OH gms.	NH <sub>3</sub> gms.	NO <sub>2</sub> gms.	Gas at N.T.P. c.c.	NO gms.	N <sub>2</sub> O gms.	N <sub>2</sub> gms.
1a	0.05	50	0.7	30	83	0.6920	0.000	0.00912	0.0246	...	...	...	...	...
1	0.10	50	0.7	30	15	0.6695	0.031	0.01873	0.01788	4.824	5.00	...	...	...
2	0.11	50	0.7	30	13	0.6664	0.033	0.02011	0.01685	5.304	5.45	...	...	...
3	0.12	50	0.7	30	11	0.6462	0.053	0.02311	0.01459	5.637	6.75	...	...	...
4	0.13	50	0.7	30	9	0.6337	0.066	0.02816	0.01390	6.096	10.10	...	...	...
5	0.14	50	0.7	30	7	0.6258	0.073	0.03268	0.01372	6.607	14.70	0.00104	0.00946	0.001434
6	0.16	50	0.7	30	6	0.5808	0.1185	0.02561	0.01456	7.523	18.10	0.00124	0.01030	0.002610
7	0.18	50	0.7	30	6	0.5698	0.1285	0.01890	0.01512	8.480	...	...	...	...
8	0.20	50	0.7	30	5	0.5546	0.1440	0.01650	0.01518	9.614	28.25	0.00277	0.01581	0.003779
9	0.25	50	0.7	30	4	0.5220	0.1770	0.01550	0.01475	11.228	31.30	0.00292	0.02155	0.004501
10	0.30	50	0.7	30	4	0.4926	0.2056	0.01420	0.01363	13.850	34.80	0.00274	0.02435	0.004968
11	1.40	50	0.7	30	1.5	0.00	0.6930	0.0000	0.000	...	Large volume of gas. Excess of NO.			

TABLE II.

Reaction between nitric acid and tin. (Varying temperature of reaction).

Experi- ment No.	HNO <sub>3</sub> Conc. g/c.c.	Acid c.c.	Tin grms.	Temperature °C.	Time Minutes.	Sn grms.	Sn grms.	NH <sub>4</sub> OH grms.	NH <sub>3</sub> grms.	NO <sub>2</sub> grms.	Gas at N.T.P. C.C.
1	0.14	50	0.7	0.0	35	0.6930	0.000	0.00916	0.02214	6.730	.
2	0.14	50	0.7	10	25	0.6893	0.010	0.01318	0.01694	6.716	.
3	0.14	50	0.7	15	18	0.6847	0.015	0.01919	0.01522	6.730	3.10
4	0.14	50	0.7	20	15	0.6699	0.029	0.02511	0.01418	6.699	3.10
5	0.14	50	0.7	30	7	0.6258	0.073	0.03268	0.01372	6.607	14.70
6	0.14	50	0.7	32	7	0.6219	0.075	0.03125	0.01413	6.653	16.50
7	0.14	50	0.7	34	7	0.6130	0.085	0.03011	0.01418	6.655	16.40
8	0.14	50	0.7	36	6	0.6073	0.091	0.02901	0.01453	6.708	..
9	0.14	50	0.7	40	6	0.5866	0.111	0.02710	0.01453	6.708	16.60
10	0.14	50	0.7	70	3.5	0.00854	0.690	0.02113	0.00692	6.699	Large
11	0.14	50	0.7	100	1.5	0.0011	0.695	0.01007	0.00173	6.658	Volume

TABLE III.  
Reaction between nitric acid and tin. (Varying amount of tin).

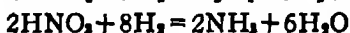
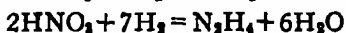
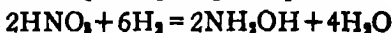
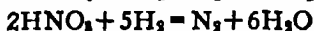
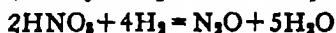
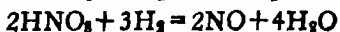
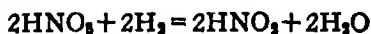
Experiment No.	HNO <sub>3</sub> Conc. g/c.c.	Acid c.c.	Tin grams.	Temperature °C.	Time Minutes.	Sn. gms.	Sn. gms.	NH <sub>2</sub> OH gms.	NH <sub>3</sub> gms.	NO', gms.	Gas at N.T.P.	NO gms.	N <sub>2</sub> O gms.	N <sub>2</sub> gms.
1	0.14	50	0.35	30	4	0.3112	0.0361	0.01315	0.00813	6.651	8.5	...	..	...
2	0.14	50	0.70	30	7	0.6258	0.0730	0.03258	0.01372	6.607	14.7	0.00105	0.00946	0.001434
3	0.14	50	1.40	30	15	1.1850	0.2160	0.06029	0.02808	6.680	25.75	0.00187	0.02149	0.002538
4	0.14	50	2.10	30	25	1.807	0.301	0.09450	0.04101	6.135	36.10	0.00294	0.02930	0.003031
5	0.14	50	2.80	30	45	1.841	0.941	0.14390	0.06634	6.074	...	...	...	...
6	0.14	50	3.50	30	60	2.245	1.235	0.1767	0.08545	5.855	...	...	...	...

mixture, containing nitrous oxide and nitrogen was exploded with hydrogen, and the contraction in volume gave a measure of the amount of nitrous oxide present.

#### *Discussion.*

Dhar holds that nitric acid oxidises metals in exactly the same way as it oxidises substances such as sugar, starch etc. (Jour. Phys. Chem 29, 142, 1925). Clearly the hydrogen theory of Ackworth and Armstrong cannot be applied to these latter substances. The undoubted similarities between the two cases are not sufficient to justify Dhar's general statement, as is shown by the various behaviours of different metals towards nitric acid. Dhar agrees with the view of Divers (Jour. Chem. Soc. 43, 465, 1883) that metals fall into two groups with respect to their reaction with nitric acid, the first group (copper, mercury, silver, etc.) do not give rise to hydrogen at any stage of the reaction but take up oxygen from the acid. The second group (iron, tin, zinc etc.) not only take up oxygen, but may even add hydrogen to the acid. There can be no real similarity between this latter behaviour and that of starch etc. Thus Dhar's theory cannot apply to the second group of metals, so that for these we must hold to the hydrogen theory. The argument that the hydrogen has insufficient time to carry out the reduction does not apply, because it is in the nascent state and therefore of great activity. Furthermore, the oxidation theory does not account satisfactorily for the formation of hydroxylamine, ammonia etc., at least in this reaction (as tin has no action on water at ordinary temperatures), and so it seems reasonable to suppose that the hydrogen produced is responsible for the reduction of the excess acid.

If the reduction of nitric acid be attributed to nascent hydrogen, the following equations would represent the process of formation of the various products :



The formation of these products should not be supposed to take place directly, however, for there will be a series of intermediate stages which are not shown.

In the present experiments, the hydrogen necessary for the formation of the reduction products was calculated from the above equations, and was compared with the total quantity of hydrogen which tin is capable of producing when it dissolves in nitric acid. These two

TABLE IV.

Hydrogen necessary for the reduction products (Table I-III) compared with the hydrogen available from tin.

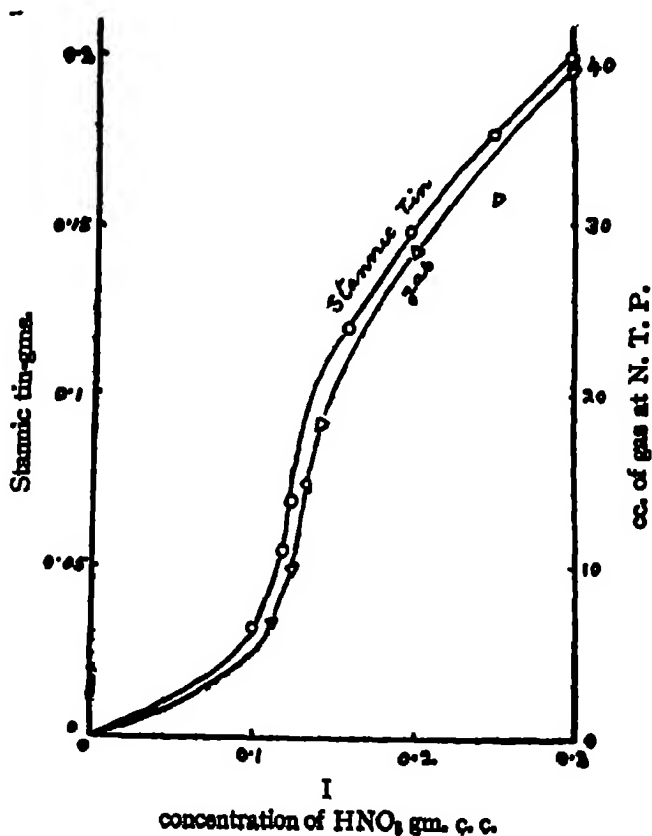
Table No.	Expt. No.	H <sub>2</sub> for NH <sub>4</sub> OH gms.	H <sub>2</sub> for NH <sub>3</sub> gms.	H <sub>2</sub> for NO gms.	H <sub>2</sub> for N <sub>2</sub> O gms.	H <sub>2</sub> for N <sub>2</sub> gms.	H <sub>2</sub> from Stannous tin gms.	H <sub>2</sub> from Stannic tin gms.	Total H <sub>2</sub> for the products gms.	Total H <sub>2</sub> from tin taken gms.
I	8	0 002998	0 007188	0 0002773	0 002898	0 001268	0 009419	0 004891	0 01482	0 014310
I	9	0 002616	0 006485	0 0002644	0 003947	0 001619	0 008865	0 006912	0 01493	0 014880
I	10	0 002580	0 006381	0 0002768	0 004460	0 001788	0 008366	0 006984	0 011548	0 011535
II	*2	0 002414	0 008007	..	..	..	0 01170	0 00034	0 01042	0 01204
II	*3	0 003519	0 007209	..	..	..	0 01162	0 00051	0 01073	0 01213
II	*4	0 004601	0 006716	..	..	..	0 01138	0 000985	0 01131	0 01236
III	2	0 005936	0 006497	0 0001052	0 001733	0 0005158	0 010630	0 002485	0 014750	0 013120
III	3	0 013270	0 011040	0 0001888	0 003936	0 0009163	0 020130	0 007336	0 029350	0 027466
III	4	0 01730	0 019420	0 0002963	0 005367	0 0010940	0 03068	0 010220	0 043477	0 04090

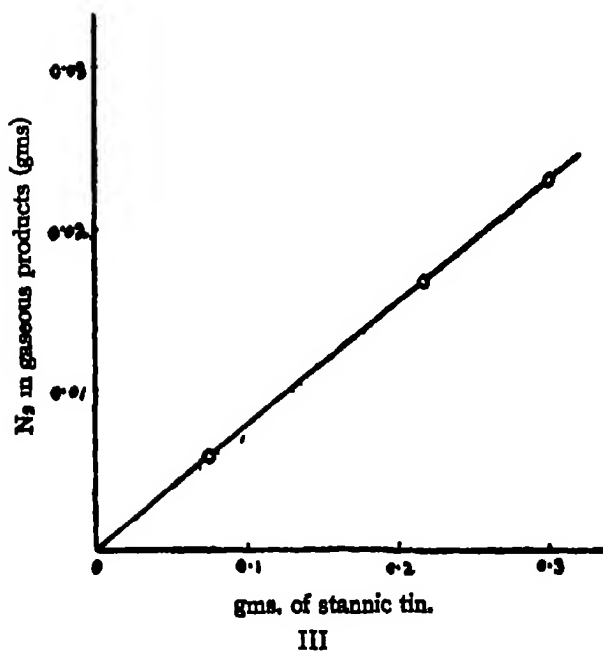
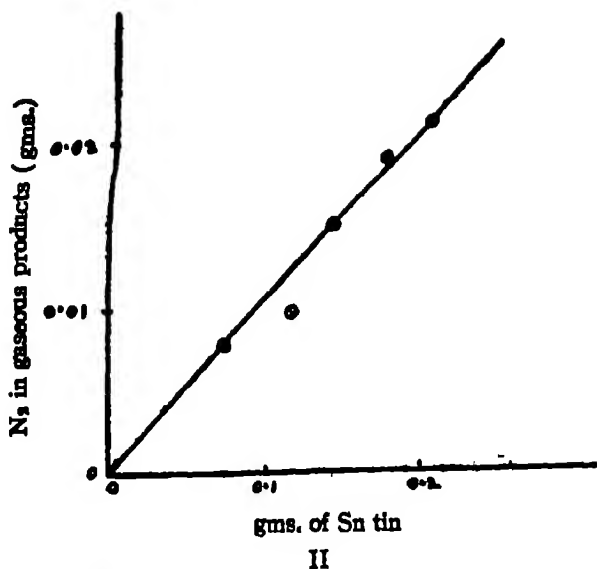
\* In these experiments the gaseous products of the reaction were not analysed.

calculated values were found to be in excellent agreement (Table IV). This suggests that all the hydrogen necessary for the reduction of the excess nitric acid probably arises from the solution of the tin. Therefore, although the oxidation theory is not conclusively disproved, it is reasonable to conclude from the above that the view of Ackworth and Armstrong is correct as far as this reaction is concerned.

It is also interesting to observe that with increase of concentration of the acid, or of the temperature, the amounts of stannic salt, and the gaseous products, increase, and the amount of the reduction products in solution (hydroxylamine etc.,) decreases.

When the amount of stannic tin, and the volume of the gaseous products, are each plotted against the concentration of the acid (Graph I), the curves are found to be practically parallel. Also when the amount of stannic tin is plotted against the nitrogen content of the gaseous mixture, straight lines are obtained (Graphs II and III). It is clear then that there is a close relationship between the formation of stannic tin and that of the gaseous products.



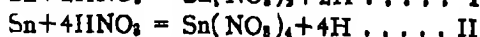


At high temperatures or concentrations only stannic tin is formed, and there is a proportionate evolution of gas. At low temperatures or concentrations very little stannic tin is formed, and accordingly the gaseous products are negligible in amount.



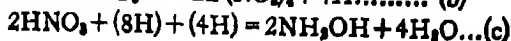
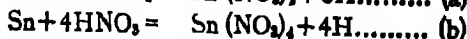
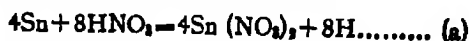
Thermochemical data show that the formation of the stannous ion from tin involves an evolution of about two-thirds the heat evolved by the formation of the stannic ion. Nitrogen-hydrogen compounds are exothermic, whereas nitrogen oxygen compounds are endothermic. It may therefore be assumed that the formation of nitrogen-oxygen compounds are associated with the formation of stannic ion, and that of nitrogen hydrogen compounds with that of stannous ion.

It may be assumed that the nascent hydrogen produced by the action of tin on nitric acid is of two different activities, an assumption which is suggested by the results of others on the activity of nascent hydrogen (Comp Treatise on Inorganic Chem. Mellor. Vol. I, p. 332). One variety of nascent hydrogen could cause the formation of the nitrogen hydrogen compounds, and the other that of the nitrogen-oxygen compounds. These two varieties may arise in accordance with the following equations —

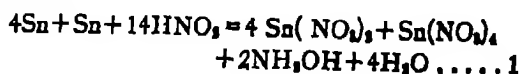


The hydrogen from the first of these reactions would cause the formation of the nitrogen hydrogen compounds, and that from the second of the nitrogen oxygen compounds, thus accounting for the proportionality between the amounts of stannous tin and the nitrogen-hydrogen compounds on the one hand and those of stannic tin and the nitrogen oxygen compounds on the other.

A closer inspection of the results shows that in all the experiments where hydroxylamine was formed, and the amount of gas evolved was negligible, an appreciable amount of tin was present in the stannic condition. If all the reduction products of nitric acid are arranged in their order of reduction, hydroxylamine is found to be between nitrogen and hydrazine. Since hydroxylamine is on the border line between the nitrogen hydrogen and nitrogen-oxygen compounds, it seems probable that the combined action of both varieties of nascent hydrogen would account for its formation. On this view the formation of hydroxylamine may be represented as follows :



Therefore,

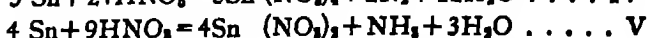
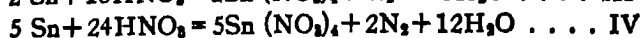
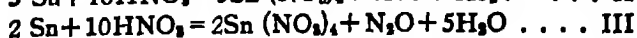
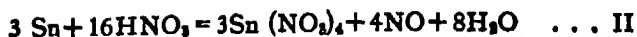


The formation of the other products, which are a result of the reduction of the acid by hydrogen of a single activity, may be represented as follows :—

TABLE V.

Stannous and stannic tin, calculated from the suggested equations and compared with the experimentally determined stannous and stannic tin.

Table No.	Experiment No.	Sn for $\text{NH}_4\text{OH}$ gms.	Sn for $\text{NH}_4$ gms.	Sn for $\text{NH}_4\text{OH}$ gms.	Sn for NO gms.	Sn for $\text{N}_2\text{O}$ gms.	Sn for $\text{N}_2$ gms.	Sn Calculated gms.	Sn exptal. gms.	Sn Calculated gms.	Sn exptal. gms.
I	5	0.2324	0.3784	0.0581	0.003063	0.05046	0.01503	0.6108	0.6258	0.1266	0.073
I	6	0.1821	0.4017	0.04550	0.003647	0.05493	0.02734	0.5838	0.5808	0.1314	0.1185
I	8	0.1173	0.4187	0.02932	0.008137	0.08433	0.03959	0.5360	0.5540	0.1613	0.1440
I	9	0.1118	0.4069	0.02795	0.007700	0.1149	0.04715	0.5187	0.5220	0.1977	0.1770
I	10	0.1009	0.3760	0.02523	0.008058	0.1299	0.05205	0.4769	0.4926	0.2152	0.2056
III	2	0.2324	0.3784	0.0581	0.003063	0.05046	0.01503	0.6108	0.6258	0.1266	0.0730
III	3	0.4286	0.7747	0.1072	0.005498	0.1147	0.02659	1.2033	1.1850	0.2540	0.2160
III	4	0.6719	1.132	0.1679	0.008626	0.1584	0.03175	1.8039	1.807	0.3636	0.3010



To test these equations, they were used to calculate the amounts of tin which must dissolve to the stannous and the stannic condition to give the observed reduction products. These amounts were then compared with the experimental values. Table V shows that the agreement is good.

The above equations can thus be accepted as representing the processes of reduction of the excess nitric acid.

Further investigation is now in progress, with a view to determining the intermediate stages of the reaction.

#### *Summary.*

The reaction between tin and nitric acid under varying conditions has been studied by estimating all the products formed during the reaction, both in the dissolved and in the gaseous state. It has been shown that during the reaction in addition to the formation of stannous and stannic salts, hydroxylamine, ammonia, nitric oxide, nitrous oxide, and nitrogen are formed. Neither nitrous acid nor hydrazine were formed under the conditions studied.

It has been pointed out that the variations in the stannic tin and the gaseous reduction products of excess nitric acid go hand in hand; likewise the variation of stannous tin in solution and the variation of the reduction products in solution, namely hydroxylamine etc.

In an attempt to explain the reduction of excess nitric acid not only has it been shown that nascent hydrogen is the probable reducing agent, but it has further been suggested that the nascent hydrogen produced by the dissolution of tin in nitric acid may be of two different activities, the dissolution of tin to the stannous condition producing hydrogen of one activity, and the dissolution of tin to the stannic condition producing hydrogen of another activity.

*Chemistry Laboratory*

*Wilson College, Bombay*

*1st July, 1933.*

## A NOTE ON CATALYSIS IN THE PYROLYSIS OF HYDROCARBONS

*By*

T. S. WHEELER

The increasing number of technical processes which involve the heat treatment of hydrocarbons, such as the liquid and vapour phase cracking of oils, and the pyrolysis and polymerisation of hydrocarbon gases, has necessitated the development of special heat and corrosion resisting alloys as reaction plant materials. The choice of a suitable material for any particular process requires an understanding of the catalytic rôle played by these alloys in the decomposition of hydrocarbons. This probably takes place with the elimination of hydrogen and the formation of fugitive unsaturated groups which either polymerise or further decompose.

In the application of these processes it is essential that the material of the reaction plant should be such as will inhibit the decomposition of the hydrocarbon to carbon and hydrogen only. A good "anti-catalyst" for the decomposition is required.

The following theory regarding the catalytic properties of metals and metallic alloys in the presence of hydrocarbons at high temperatures has been evolved by the author, and serves as a qualitative guide in the choice of plant materials for such reactions.

The basis of the theory is that catalytic activity in the heterogeneous reactions under consideration depends upon the presence of loosely bound electrons on the surface of the catalyst. These form centres of intense activity around which decomposition reactions vigorously occur. Conversely the absence of such energising centres inhibits chemical activity. To illustrate these remarks we may mention the activity of iron in promoting complete decomposition of hydrocarbons to carbon and hydrogen. This is to be referred to the presence of mobile electrons.

Now compounds such as silica with a stable electronic structure do not catalyse directly the decomposition of hydrocarbons to carbon and hydrogen. R. V. Wheeler and Wood (*Fuel*, 9,567, 1930) have shown that alloy steels behave in this respect like silica. This leads to the idea that the high electrical resistance of these alloys is due to the fact that the electrons are not mobile. We note in this connection that the following properties are common in certain alloys.—(1) High

electrical resistance, (2) low thermal conductivity, (3) High melting point, (4) High tensile strength, (5) A high hardness number (6) High resistance to the action of chemicals, and that all may be referred to the stability of electron groups.

If therefore we correlate these properties with the anti-catalytic action we see that the electrical resistance of an alloy may serve as an index of the lack of mobility of the electrons, and hence of the anti-catalytic properties in the decomposition of hydrocarbons

With regard to the metals which alloyed with iron give suitable alloys, it should be noted that all the elements of value as additions to iron in the production of alloy-steels lie at or near the minima of the curve of atomic volumes plotted against atomic number. It is logical therefore to expect that the elements of low atomic weight lying at the first and second minima, beryllium, boron and aluminium may prove of value in the production of alloy steels and also of anti-catalytic materials.

## A SIMPLIFIED METHOD FOR THE PREPARATION OF ANILIDES

By

R. C. SHAH and R. K. DESHPANDE.

The preparation of an anilide from a carboxylic acid is a common operation in organic chemistry. It is usually carried out in two ways —

- (1) By heating the acid and the aniline together at a high temperature. This is a tedious process and takes a long time and the yields are not always satisfactory.
- (2) Through the acid chloride, the acid being converted into the acid chloride by the action of phosphorus pentachloride. The acid chloride has to be separated from the other product of the reaction *viz.* phosphorus oxychloride, which is removed by distillation under reduced pressure, before it can be utilised for the preparation of the anilide. This is essential as phosphorus oxychloride, if present, would itself react readily with the aniline, giving compounds like  $C_6H_5NH.POCl_2$ ,  $CH_3NH.PO.O = NPh$ , and  $(C_6H_5NH)_2PO$ . (Cf. Mich and Schultze, *Ber.*, 26, 2939, Mich and Silberstein, *ibid.*, 29, 720; *Annalen*, 326, 245, Mich and Soden, *Annalen*, 229, 339).

Thus a method is lacking whereby an acid can be readily converted into an anilide.

Barnett (*Chem. News*, 1926, p. 190) has described a method for the preparation of anilides wherein 1 mol. of the acid and 1 mol. of the amine are dissolved in 2 to 3 parts of pyridine, the mixture cooled in a freezing mixture and thionyl chloride slowly added. After keeping for some time, the mixture is poured into water and the precipitated anilide filtered and purified. No quantitative mention is made of the yields obtained by this method, it being merely stated that very good results were obtained with some acids and that the method failed in some cases.

In connection with investigations on the chemistry of anilide-imido-chlorides which have been in progress in these laboratories for some time, the authors had occasion to prepare a large number of anilides. Several attempts were made to devise a simplified method for

the purpose, and ultimately the following simple and quick method for the preparation of anilides was worked out.

The method consists in the addition of dimethyl-aniline, diethyl-aniline or pyridine to the crude mixture of the acid chloride and phosphorus oxychloride, obtained by the action of phosphorus pentachloride on the acid, and subsequent addition of the amine to the well cooled mixture.

The method considerably simplifies the preparation of anilides, as it does away with the tedious process of the removal of phosphorus oxychloride and the isolation of the acid chloride. As will be seen from the experimental portion, high yields almost as good as those by the use of pure acid chlorides, can be obtained by this method.

The success of the method is doubtless due to the fact that the tertiary amine greatly promotes the reaction between the aniline and the acid chloride, which thus preferentially reacts, to the almost complete exclusion of phosphorus oxychloride from reaction.

The general applicability of the method has been established by testing it with a number of acids, mostly aromatic, and different types of primary and secondary aromatic amines.

An attempt to extend the method to the preparation of esters was unsuccessful, low yields being obtained.

The method is well adapted for the preparation of anilides, either in small quantities for characterising acids, or in quantity for other work.

## EXPERIMENTAL.

### *General Method.*—

The mixture of the acid chloride and the phosphorus oxychloride, obtained by the action of phosphorus pentachloride on the acid (1 mol.), is cooled, preferably in a freezing mixture, and dimethyl-aniline, diethyl-aniline, or pyridine (2 mols) added in small portions. The amine (1.2-1.5 mols) is then added gradually, with stirring to the cooled mixture. With the progress of the reaction which is very rapid, the mixture usually thickens considerably, and sometimes solidifies towards the end. By treating the product successively with dilute hydrochloric acid, dilute sodium hydroxide and finally with water, the anilide is obtained fairly pure, and may be further purified by crystallisation if necessary.

TABLE I.

The following anilides were prepared by this method from different acids by the action of aniline.

Anilide.	Yield of the pure crystallised product. % of Theory.	M P.	M P. given in literature.
Benzanilide	90%	162°	163°
p-nitrobenzanilide	85%	216°	213°
m-nitrobenzanilide	80%	155°	154°
o-nitrobenzanilide	75%	154°	155°
o-chlorobenzanilide	80%	114°	114°
p-bromobenzanilide	80%	205°	197°
Anisanilide	80%	169°	168-169°
$\alpha$ -naphthanilide	85%	160°	160°
$\beta$ -naphthanilide	85%	167°	170°
Cinnamanilide	70%	149°	150°
Trichloroacetanilide	80%	94°	94°

TABLE II.

The following benzoyl compounds were prepared from various primary and secondary aromatic amines and benzoic acid.

Compound.	Yield of the pure crystallised product % of theory.	M.P.	M.P. given in literature.
benzoyl-o-nitraniline	75%	93°	94°
" " -m-nitraniline	80%	155°	155°
" " -p-nitraniline	80%	197-198°	199°
" " -o-toluidine	75%	142°	143°
" " -m-toluidine	80%	126°	125°
" " -p-toluidine	85%	157°	158°
" " -diphenylamine	75%	178-179°	180°
" " $\alpha$ -naphthylamine	80%	159°	160°
" " $\beta$ -naphthylamine	80%	162°	162°
" " -Phenylhydrazine	75%	168°	168°
" " -thiodiphenylamine	80%	163°	165°
dibenzoyl-o-phenylenediamine	70%	295-298°	301°

The authors are thankful to Dr. A. N. Meldrum for his kind interest in the work.

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**DERIVATIVES OF SALICYLIC ACID—PART VII.**  
**INTERACTION OF THIONYL-CHLORIDE WITH ESTERS**  
**OF AROMATIC HYDROXY ACIDS IN THE PRESENCE**  
**OF FINELY DIVIDED COPPER.**

**PART—II.**

**SYNTHESIS OF THIO-ETHER OF 4-METHOXY**  
**SALICYLIC ACID AND RELATED COMPOUNDS.**

*By*

**N. W. HIRWE**

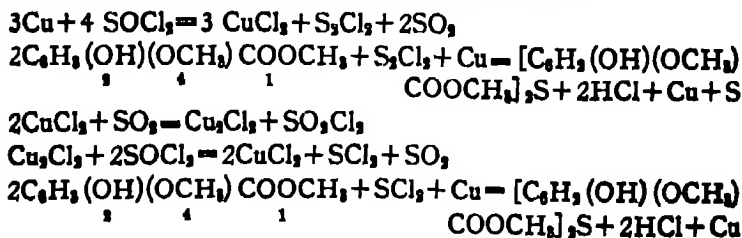
**G. V. JADHAV**

**Y. M. CHAKRADEO**

The methyl ester of 4-methoxy salicylic acid was found to be a suitable substance to continue the study of the interaction of thionyl chloride with esters of aromatic hydroxy acids in presence of finely divided copper, described in the Derivatives of Salicylic acid Part VI ---Interaction of thionyl chloride with aromatic hydroxy acids in the presence of finely divided copper Part I Synthesis and constitution of thio-ether of salicylic acid and related compounds. (Journal American Chemical Soc) (insert ref. when published)

Esters have been specially chosen in order to control the formation of anhydrides which occurs with O-hydroxy benzoic acids in presence of thionyl chloride

With methyl salicylate it has been shown that the reaction is catalytic and continuous as long as the sulphur dioxide liberated in the reaction is made available. The following equations with 4-methoxy methyl salicylate give the different stages in the reaction:—

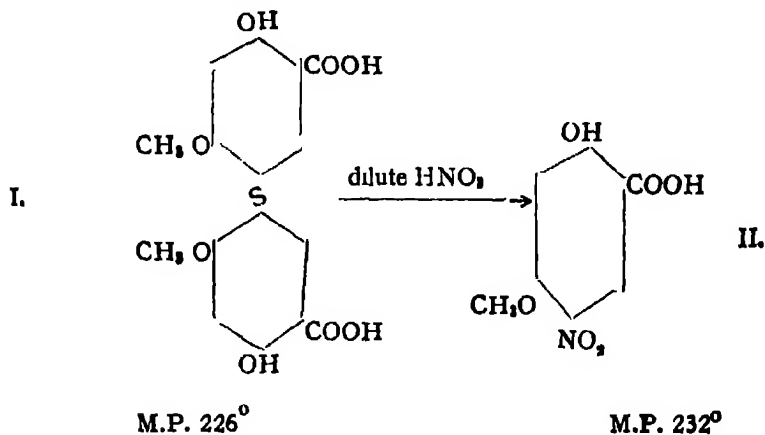


The above scheme represents the mechanism truly because (i) copious fumes of sulphur dioxide and hydrogen chloride are evolved; (ii) Free sulphur is found in the reaction mixture (iii) Sulphur mono-chloride and sulphur dichloride give the desired sulphides when used in the presence of finely divided copper, and (iv) The reaction which is

absent in the presence of anhydrous cupric chloride begins on passing  $\text{SO}_2$  into the reaction mixture and a good yield is obtained. Addition of water to the reaction mixture containing anhydrous cupric chloride or use of hydrated cupric chloride affects the reaction favourably.

It is interesting to note that the additional hydroxy group in the 4-hydroxy methyl salicylate (methyl  $\beta$ resorcyate) adds to the vigour of the reaction, so that it becomes uncontrollable and no crystalline product can be isolated, while the reaction progressed smoothly on converting it to methoxy.

Formation of acetyl and benzoyl derivatives shows that the  $-\text{OH}$  group is free and the linking is nuclear. When the comp. (thio-ether) is heated hydrogen sulphide is evolved, this supports the sulphide structure. The probability due to orienting influences in the molecule is that the sulphur links in-5 position. This is confirmed by nitration of comp. I with dilute nitric acid to give comp II which is identical with the 4-methoxy 5-nitro salicylic acid described by Gilbody and Perkin (J Chemical Soc 1902, 81, 1056).



### EXPERIMENTAL.

#### *Bis-3-carbomethoxy-4-hydroxy-6-methoxy phenyl thio-ether* —

The methyl ester of 4-methoxy salicylic acid (35g) was mixed with thionyl chloride (50g.) and copper dust (20g) was gradually added to it, when dense fumes of hydrogen chloride and sulphur dioxide were evolved. The reaction-mixture was protected from moisture by means of a cork carrying a glass-tube bent twice at right angles instead of the usual calcium chloride tube. The mixture was left at room-temperature overnight and then warmed on water-bath for some time. The mixture was then extracted with hot chloroform and filtered from copper dust. On evaporation of the solvent a pasty solid was left be-

hind which was washed with petroleum ether and crystallised from dilute acetic acid in colourless needles. It is insoluble in water and petroleum ether and soluble in benzene, acetic acid, acetone, methyl and ethyl alcohols, and carbon disulphide. It gives bluish violet colouration with ferric chloride solution (Found S, 8.2; equivalent 196.8;  $C_{18}H_{18}O_8$  S requires S 8.1 per cent. equivalent 197.0).

*Bis-3-carboxy-4-hydroxy-6-methoxythio-ether*

The ester (10g) was treated with 10 per cent. sodium hydroxide solution (100c.c.) and boiled with a reflux condenser for about two hours. The solution was then treated with dilute hydrochloric acid when a solid separated which was washed with water and crystallised from glacial acetic acid in colourless plates, m. p.  $226^{\circ}$ . It is insoluble in water, dilute acetic acid and petroleum ether and soluble in acetone, ethyl and methyl alcohols and glacial acetic acid, and difficultly soluble in chloroform and benzene. It gives bluish violet coloration with ferric chloride solution (Found S, 8.4, equivalent 183.2,  $C_{18}H_{16}O_8S$  requires S, 8.74 per cent. and equivalent 183.0.)

*Sodium salt*

Sodium salt of bis-3-carboxy-4-hydroxy-6-methoxy thio-ether was prepared by neutralising the acid with sodium hydroxide solution. It was evaporated to dryness on a water-bath and recrystallised from dilute alcohol as it is easily soluble even in cold water. It crystallises in colourless needles. (Found Na, 10.6,  $H_2O$  3.9,  $C_{18}H_{12}O_8SNa_2$ ,  $H_2O$  requires Na, 10.75,  $H_2O$ , 4.2 per cent.)

*Potassium Salt*

This was prepared by neutralising the acid with potassium hydroxide solution. It was then evaporated to dryness on a water-bath. It is fairly soluble in hot water from which it is recrystallised as colourless needles. (Found K, 16.1,  $H_2O$ , 7.4,  $C_{18}H_{12}O_8SK_2$ ,  $2H_2O$  requires K, 16.3, and  $H_2O$ , 7.5 per cent.)

*Calcium Salt*

This was prepared by first neutralising the acid with ammonium hydroxide solution and then adding calcium chloride solution to it. The precipitate was filtered, washed and recrystallised from hot water as colourless needles. (Found Ca, 8.2;  $H_2O$ , 14.9;  $C_{18}H_{12}O_8SCa$ ,  $4H_2O$  requires Ca, 8.4 and  $H_2O$ , 15.1 per cent.)

*Barium Salt*

This was prepared by treating the ammonium salt solution of the thio ether with the solution of barium acetate when the barium salt was precipitated. It was washed, and recrystallised from hot water as colourless needles (Found. Ba, 23.7,  $H_2O$ , 12.7;  $C_{18}H_{12}O_8SBa$ ,  $4H_2O$  requires Ba, 23.9; and  $H_2O$ , 12.6 per cent.)

*4-methoxy-5-nitro salicylic acid* .

Bis-3-carboxy-4-hydroxy-6-methoxy phenyl thio-ether (2g.) was treated with dilute nitric acid (20ccs. of Nitric acid (Sp. Gr. 1.45) and, 80 ccs. of water) and the mixture warmed till a colourless solution was obtained. The mixture was diluted with water and the solid obtained was washed and recrystallised from dilute alcohol in colourless needles. m. p.  $232^{\circ}$ . (Found N, 6.4,  $C_8H_7O_6N$  requires N, 6.6 per cent.) Gilbody and Perkin (Jour. Chem. Soc. 1902, 81, 1056) give m. p.  $230^{\circ}$ .

*Bis-3-carbomethoxy-4-acetoxy 6-methoxy phenyl thio-ether* .

Bis-3-carbomethoxy-4-hydroxy-6-methoxy phenyl thio-ether (2g) was gradually added to acetic anhydride (13g) containing a few drops of concentrated sulphuric acid. The mixture was gently warmed till a clear solution was obtained. It was then poured over crushed ice and the solid obtained was washed and recrystallised from alcohol in colorless needles m. p.  $162^{\circ}$ . It is soluble in acetic acid, chloroform, acetone and ethyl and methyl alcohols, insoluble in water, benzene and petroleum ether. (Found S, 6.4,  $C_{22}H_{22}O_{10}S$  requires S, 6.7 per cent.)

*Bis-3-carbomethoxy-4-benzoyloxy-6-methoxy phenyl thio-ether*

Bis-3-carbomethoxy-4-hydroxy-6-methoxy phenyl thio-ether (1.5g.) was dissolved in pyridine and benzoyl chloride (5g) was gradually added to it. The mixture was refluxed on a water-bath for about three hours. On pouring the solution over crushed ice a liquid separated which slowly solidified on repeated washing with ice-cold water. It was crystallised from alcohol in colourless needles, m. p.  $185^{\circ}$ . (Found S, 5.2,  $C_{22}H_{20}O_{10}S$  requires S, 5.3 per cent.)

*Bis-3-carbamido-4-hydroxy-6-methoxy-phenyl thio ether*

Bis-3-carbomethoxy-4-hydroxy-6-methoxy phenyl thio-ether (4g) was put into liquor ammonia (100 ccs.) and the mixture was mechanically shaken for about eight hours, when a clear solution was obtained. The solution was evaporated on a water-bath and the solid was crystallised from boiling glacial acetic acid, in gritty flakes m. p.  $187^{\circ}$  with decomposition. It is practically insoluble in most of the common organic solvents. (Found N, 7.4, S, 8.6,  $C_{16}H_{16}O_6N_2S$  requires N, 7.7 and S, 8.8 per cent.)

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# THE EFFECT OF TEMPERATURE IN FERROMAGNETIC CRYSTALS

by

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"Nous avons déduit des propriétés des lignes d'égale aimantation —(in the H-T plane)—l'impossibilité d'une équation d'état ferromagnétique, fondée sur la loi classique du paramagnétisme et sur celle du champ moléculaire, et nous avons reconnu la nécessité de retoucher les postulats fondamentaux "

—Weiß et Forrer [*Ann. de Phys.* Jan-Février 1926  
Tome V, page 153]

"The results of experiments do not appear to be in agreement with the Weiß theory of specific heats of Ferromagnetic substances."

—"Specific Heats of Ferromagnetic Substances" by  
Sucksmith and H H Potter, *Proc. Roy Soc.*  
Vol 112, 1926, p. 176.

## [1°] *The scope of the present Paper and some introductory remarks*

A brief summary of the writer's first paper\* was published in the *Proc. Cambridge Phil Soc*, Vol 23, pt 2, and the main criticism of the work came from Debye and Pauli in an informal conference on Magnetism held at Zürich. It was to the effect that the concept of temperature was neglected and that the problem was treated as simply a geometrical, statical one.

The object of the present paper is to take account of Temperature effects, and to revise and consolidate in that light some of the main results obtained before. The exact bearing of the quotations at the top will become clear when we shall come to explain Weiß's latest experiments (1926) on theoretical grounds.

It may be recalled here for the sake of definiteness, that in the previous paper, on the assumptions that

(i) elementary molecular magnets in a ferromagnetic crystal are nothing but atoms with magnetic properties due to the presence of electronic orbits,

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\* Published in *extenso* as "A Contribution to the Theory of Ferromagnetic Crystals." *Phil. Trans. Roy Soc London*, Series A, Vol. 228, pp 63-114. (1929).

(ii) that in a "space-centred" structure,—whether cubic or non-cubic,—the atoms split themselves, in any steady state, into two groups with two distinct directions for their magnetic axes. The two groups severally belong to the two component simple lattices. The two directions coincide for saturation, and are exactly opposite for the unmagnetised state,

we found that,—

(iii) Webster's experimental results could be explained theoretically, without postulating the existence of any 'molecular field', but simply with the aid of the 'atomic actions'.

It was also shown that—

(iv) 'the atomic actions' could be effectively substituted for by a molecular field according to a general law, which included both the cubic and the non cubic cases,—and which in the particular non cubic case (of Pyrrhotite) reduces to Weiss's law of 'simple proportionality'.

Now, out of these four items, it is only (ii), the assumption of 'two groups', that is going to be replaced in this section. And as it was used only in the third section dealing with non saturated states its revision does *not* affect our main results, as they referred to Saturation states

The grounds for revision are mainly three —

1. It is plausible in the case of a "space centred" structure, where we have exactly two simple component lattices, but what about 'simple', or 'face centred' structures? There is no definite way of dividing the atoms into two groups.

2 The second is now a theoretical objection to some extent writing in 1925, L. W. McKeenhan says,

"It appears after a little study of the older theories that none of them have taken sufficient notice of the fact that the medium, the behaviour of which they attempt to describe is really discontinuous. Some of the theories are quite obviously faulty in this respect, introducing intrinsic fields of force to a greater or less extent, and thereby avoiding consideration of the physical basis of magnetic retentivity and hysteresis. Others begin with the atoms but introduce what amounts to the assumption of a continuous medium when groups of atoms are pictured as undergoing simultaneously equal changes in magnetization"

—*Phys. Review* 1925, Vol 26, page 275

It will be observed that this criticism is as much directed against our assumption of 'two groups', as it is against Weiss's molecular field. McKeenhan suggests in his paper that the magnetizing process in a body must proceed discontinuously in space as well as in time. Now, it is not impossible to reply to McKeenhan's criticism if the group-assumption were really found indispensable. But, as will be seen,

3. the way in which the concept of Temperature is to be introduced, renders it unnecessary to maintain,

Conversely, also, if the assumption is given up, temperature must come in to explain the existence of states other than that of Saturation.

[2°] *A historical Note*—

In his article on "Para-and-diamagnetism" in [*Bull. Nat. Res. Council*, Vol. 3, part 3 p. 68 (1922)], Wills has summarised the various attempts to introduce temperature and derive the "equation of magnetic state" of a substance—i.e. to say to correlate in a relation temperature, applied field, and magnetization, viz.

$$f(H, T, \sigma) = 0.$$

A few points, however, need to be noted here, so as to make it clear wherein the contribution of this paper lies

1. Langevin was the first in the field. He introduced temperature as in the usual Boltzman-Maxwell statistical way, and obtained the equation of magnetic state for a paramagnetic substance in the form

$$\sigma - \sigma_0 \left( \cosh \alpha - \frac{1}{\alpha} \right), \quad \alpha = \frac{\mu H}{RT}$$

2. This relation if written in the form

$$\text{Magnetization} = \sigma = \phi \left( \frac{H}{T} \right),$$

bears close resemblance to the equation of state of an ideal gas, viz.  $p v = RT$ ; or

$$\text{density} = f \left( \frac{p}{T} \right).$$

Now, by taking account of internal pressure, Van der Waal obtained the equation of state which included liquids as well. By analogy, Weiß introduced the concept of an internal (moleculaire) field, and obtained the equation of magnetic state for ferromagnetic substances as well, in the form

$$\sigma = \phi \left( \frac{H + H_m}{T} \right)$$

[This result, as we shall come to consider more fully later, is contradicted by his latest experiments. 1926.]

3. Many of the experimental facts since Langevin's paper (1905), did not accord with the main results of his theory which were wo,—

$$\begin{cases} (i) \quad \frac{\partial \chi}{\partial T} = 0, \text{ for diamagnetic substances} \\ (ii) \quad \chi \propto \frac{1}{T}, \text{ for paramagnetic} \quad \text{''} \end{cases}$$

where  $\chi$  = susceptibility,

This led to various attempts to modify his theory. The main workers in the field have been Honda and Okubo, Gans, Oxley and Frivold. All these attempts may be grouped as those independent of Quantum hypotheses.

But, discrepancies in other directions were revealed, which necessitated the modification of Langevin's theory.—

In 1911 Nernst showed that, in contradiction to the laws of classical mechanics, the specific heats of polyatomic gases appear to decrease with decrease in temperature, and the results were ascribed to the behaviour of that portion of the specific heat which depends upon the rotation of molecules. Meanwhile, the experimental investigations of Onnes, Oosterhuis, Perrier, du Bois, Honda and Owen on the variation (with temperature) of the susceptibility of paramagnetic substances, gave results which were in opposition to equipartition theories of paramagnetism. The theory of magnetism was thus in a dilemma similar to that in which the theory of specific heat found itself.

Accordingly modifications were introduced by bringing in Quantum hypotheses. And in this connection may be mentioned the names of Oosterhuis, Keesom, Gans (again), Weyssenhoff and Reiche.

It is important to observe, however, that none of these attempts seems to consider a crystal structure, such as we have under contemplation. The principal aim of the paper, therefore, will be to introduce temperature in a way consistent with the lattice-theory of crystal-structures.

[3°] *Temperature effects in magnetic crystals to be correlated with Libration frequencies of atoms.—*

The way to introduce temperature in the present theory is somewhat similar to that which Born adopts in his "Dynamik der Kristallgitter," in dealing with specific heats of solids. There, only the translational displacements of atoms are considered, and only the corresponding frequencies are taken into account. In the present case (of ferromagnetic crystals), since the atoms have associated with them a privileged direction,—viz. the axes of their magnetic moments,—it is necessary to introduce Librational frequencies. Thus in place of Born's—

"Die potentielle Energie zwischen einer Partikel der Basis und einer andern, beide in Gleichgewichtslagen, hat den Wert,

$$\varphi \left( | r_{kk'}^{ll'} | \right) "$$

we have to write

$$\varphi \left( | r_{kk'}^{ll'} | . | \theta_{kk'}^{ll'} | . | \phi_{kk'}^{ll'} \right).$$



The notation is the same as in Born's,—

$$\mathbf{r}_{kk'}^{ll'} = \mathbf{r}_k^l - \mathbf{r}_{k'}^{l'}, \quad \text{(vector-equation).}$$

$\mathbf{r}_k^l$  denotes the vector joining the origin to the 'k'th particle in 'l'th cell.

$(\theta, \phi)$  denote the orientation of the axis of the magnetic moment of an atom. Of course

$$\left. \begin{aligned} \theta_{kk'}^{ll'} &= \theta_k^l - \theta_{k'}^{l'} \\ \phi_{kk'}^{ll'} &= \phi_k^l - \phi_{k'}^{l'} \end{aligned} \right\} \text{These are scalar equations.}$$

[It may be pointed out that so far as the purely magnetic potential energy is concerned, the  $\varphi_{kk'}^{ll'}$ -function is, (if the atoms be regarded as simple doublets),—

$$\frac{\mu_k^l \mu_{k'}^{l'}}{r_{kk'}^{ll'}{}^3} \left\{ \sin \theta_k^l \sin \theta_{k'}^{l'} \cos \phi_{kk'}^{ll'} - 2 \cos \theta_k^l \cos \theta_{k'}^{l'} \right\}.$$

Cf —Jean's *Electricity and Magnetism* p. 379

Now, first of all, neglecting T, we determine the direction of magnetization ( $\sigma$ ). Let it be  $(\theta_0, \phi_0)$ . Then we have

$$\theta_k^l = \theta_0$$

$$\phi_k^l = \phi_0,$$

To bring in Temperature, we suppose that the atoms are vibrating and their axes librating. In addition to Born's translational displacements, we have now

$$\theta_k^l = \theta_0 + \delta \theta_k^l, \quad \phi_k^l = \phi_0 + \delta \phi_k^l, \text{ \&c.}$$

Forming the equations of motion the frequencies are to be determined as in Born's articles 17 and 18. [Dynamik der Kristallgitter pp. 585-593.]

Now the  $(\theta, \phi)$ -librations reduce the average magnetic moment of the atoms in the direction about which the axes are librating, and frequencies establish a relation with the temperature, whether by the the classical equipartition formula, or by the quantum theory formula.

This is the general method of introducing the effects of Temperature, in ferromagnetic crystals.

The development of the actual algebra for this general method will be postponed for the present. In what follows the assumption of

an existence of a 'monochromatic state' will be introduced, and results obtained. Really speaking, as will be seen, this assumption is not justifiable, but it does help to give some picture of how temperature affects the various magnetic phenomena. Besides, the results obtained give a *qualitative* agreement with experiments.

[4<sup>o</sup>] *The equation Magnetic state on the assumption of a monochromatic state of libration.*—

To attack the problem of specific heats of solids, "Einstein ging von der Überlegung aus, daß die Atome eines festen Körpers als Resonatoren betrachtet werden können, dann muß aber ihre mittlere Energie durch die aus der Strahlungstheorie gewonnene Formel gegeben sein ..... Einstein vernachlässigte zuerst die Koppelungen zwischen den Atomen und schrieb diesen sämtlich dieselbe Schwingungszahl  $\nu$  zu, dann kommt den  $3N$  Freiheitsgraden eines Gramatoms die mittlere Energie

$$E = 3 R T \cdot P \left( \frac{h\nu}{kT} \right), \quad P(x) = \frac{x}{e^x - 1}."$$

In *exactly* the same way, as a first approximation the 'coupling' forces between the atoms (or say the 'librators') are now neglected, and one and the same frequency ( $\nu$ ) assumed for all.

Now let as usual,—

$\mu$  = magnetic moment of each atom

and  $\theta_0$  = maximum amplitude of any one of them for  $\theta$ -libration.

We put,  $\theta = \theta_0 \cos 2\pi\nu t$

and we get,

$$\begin{aligned} \bar{\mu} &= \frac{1}{1/\nu} \int_0^{1/\nu} \mu \cos \theta dt \\ &= \frac{1}{1/\nu} \int_0^{1/\nu} \mu \cos \left\{ \theta_0 \cos 2\pi\nu t \right\} dt \\ &= \mu \int_0^{\theta_0} (\theta_0) \end{aligned}$$

If we are dealing with low temperatures then  $\theta_0$  will be small and we can expand the integrand and neglect terms higher than  $\theta_0^3$ . Now,  $\theta_0$  will not be the same for all atoms even if  $\nu$  is the same (by assumption). The observed effect, therefore, will be to reduce the

saturation intensity  $\sigma_0$  in the ratio  $\left( 1 - \bar{\theta}_0^2/4 \right)$ .

Thus

$$\sigma = \sigma_0 \left( 1 - \bar{\theta}_0^2/4 \right).$$

Next, the mean kinetic energy due to libration is (for a single atom),

$$\frac{1}{1/\nu} \cdot \frac{1}{2} A \int_0^{1/\nu} \dot{\theta}^2 dt \\ = \frac{1}{4} A (2\pi\nu)^2 \theta_0^2$$

(A = moment of inertia of the atom about an axis  $\perp$  to its axis of magnetic moment).

The frequency  $\nu$  is determined by the equation

$$A \theta + \mu (H + H_m) \sin \theta = 0$$

Where the atom finds itself in a total field of force  $H + H_m$ . Replacing  $\sin \theta$  by  $\theta$  to our order of approximation we get, the frequency given by

$$2\pi\nu = \sqrt{\mu (H + H_m)/A}.$$

Now the mean energy of the librating atom = mean kinetic + mean potential

$$= \frac{1}{2} A (2\pi\nu) \theta_0^2 + \frac{1}{2} A (2\pi\nu)^2 \theta_0^2 \\ = \frac{1}{2} A (2\pi\nu)^2 \theta_0^2$$

$\therefore$  The mean energy for N atoms, (each vibrating with a different amplitude), is

$$\frac{1}{2} A (2\pi\nu)^2 \overline{\theta_0^2} \times N$$

By Plank-Einstein's formula we get

$$\frac{1}{2} N \cdot A (2\pi\nu)^2 \overline{\theta_0^2} = RT \cdot P \left( \frac{h\nu}{kT} \right)$$

$$\text{where } P(x) = \frac{x}{e^x - 1}$$

$$\text{i. e. } \overline{\theta_0^2} = \frac{h/2 A \pi^2}{\nu \left( e^{h\nu/kT} - 1 \right)}$$

and we get

$$\sigma = \sigma_0 \left\{ 1 - \frac{h/2 A \pi^2}{\nu \left( e^{h\nu/kT} - 1 \right)} \right\} \\ (2\pi\nu)^2 = \mu (H + H_m)/A$$

[5<sup>o</sup>] *Experimental Evidence:—*

Suppose in the first instance, that we expand the term  $e^{h\nu/kT}$ , and retain the first term, — i.e. to say adopt the classical, in place of the Quantum formula for the energy. Then we should get

$$\begin{aligned}\sigma &= \sigma_0 \left( 1 - \frac{hT/2A\pi^2}{\nu^2} \right) \\ &= \sigma_0 \left( 1 - \frac{2hT}{\mu(H+H_m)} \right) \\ \therefore (2\pi\nu)^2 &= \mu(H+H_m)/A\end{aligned}$$

Thus we have now

$$\sigma = \sigma_0 \left( 1 - \frac{2hT}{\mu \cdot H + H_m} \right).$$

This is an unsatisfactory result For, considering the order of magnitude even roughly, we have

$$h = 1.372 \times 10^{-16} \text{ erg/deg.}$$

for iron  $\mu = 10$  Weiss Magnetons  
 $= 1.8 \times 10^{-30}$

In Webster's experiments  $\begin{cases} H = 3 \times 10^3 \\ H_m = 6 \times 10^3 \end{cases}$  roughly

This means

$$\begin{aligned}\sigma &= \sigma_0 \left( 1 - \frac{2(1.3) 10^{-16} \cdot T}{1.8 \times 10^{-30} \times 3 \times 10^3} \right) \\ &= \sigma_0 [ 1 - T(10^{-1}) ]\end{aligned}$$

This would mean that the temperature must be practically zero for the formula to represent facts. For temperatures over half a degree this would give negative magnetization! But, then, we have the difficulty that at so low temperatures, the classical formula has no application.

The way out of this difficulty is suggested by the following considerations —

We had

$$\ddot{\mu} = \frac{1}{1/\nu} \int_0^{1/\nu} \cos \left\{ \theta_0 \cos 2\pi\nu t \right\} dt$$

$$\text{and } A\theta + \mu(H+H_m) \sin \theta = 0$$

In deducing from these, the results

$$\left. \begin{aligned}\ddot{\mu} &= \mu \left( 1 - \frac{\theta_0^2}{4} \right) \\ \text{and } (2\pi\nu)^2 &= \mu(H+H_m)/A\end{aligned} \right\}$$

the assumption was that  $\theta_0$  is small. Now the radiation-energy-formula has shown that  $\theta_0^2/4$  comes very great, and  $\theta_0$  cannot be treated as small, and only the first two terms will not do in the expansion of  $\cos [\theta_0 \cos 2\pi\nu t]$ ,

(i) The only way to proceed seems to be to solve the equation

$$\bar{\mu} = \frac{1}{1/\nu} \int_0^{1/\nu} \mu \cos(\theta_0 \cos 2\pi \nu t) dt$$

and  $A \dot{\theta} + \mu(H + H_m) \sin \theta = 0$

to a *greater* approximation.

(ii) The assumption of a monochromatic state is not justifiable.

(iii) The quantum formula must be adopted.

Recognizing these points, we may proceed to see the general consequences of the theory

We shall obviously get —

$$\bar{\mu} = \mu (1 - \theta_0^2/4 + \dots \&c.)$$

$$= \mu (1 - \theta_0^2 f(\theta_0^2))$$

$$\text{and } \nu = F\{(H + H_m), \theta_0\}$$

and the equation of magnetic state will be of the form .

$$\left. \begin{aligned} \sigma &= \sigma_0 \left( 1 - \overline{\theta_0^2 f(\theta_0^2)} \right) \\ \overline{\theta_0^2} &= \frac{h/2 A \pi^2}{\nu \left( e^{h\nu/kT} - 1 \right)} \\ \text{and } (2\pi\nu)^2 &= F\{(H + H_m), \theta_0\} \end{aligned} \right\}$$

Of course, for small values of  $\theta_0$  we have

$$\left. \begin{aligned} \overline{\theta_0^2 f(\theta_0^2)} &= \frac{1}{2} \theta_0^2 \\ \text{and } F &= \mu (H + H_m) / A \end{aligned} \right\}$$

*Note*—This difficulty about the order of magnitude and the necessity to solve the equation more exactly was noticed too late to correct the whole work. The exact discussion regarding Webster's curves is not possible without actually working out the results. The explanation about Weiß's curves of his latest experiments, however, holds good, all the same. The modifications will be very slight. Therefore, a very rough argument is given instead, for Weiß's curves —

In what follows, will be assumed the following form for the solution of our problem —

$$\left. \begin{aligned} \overline{\theta_0^2} &= \frac{h/2A\pi^2}{\nu \left( e^{h\nu/kT} - 1 \right)} \\ \sigma &= \sigma_0 \left\{ 1 - \overline{\theta_0^2 f(\theta_0^2)} \right\} \\ \text{and } 2\mu\nu &= \sqrt{\mu (H + H_m) / A} \end{aligned} \right\} \quad \begin{array}{l} \text{Call this a "provisional} \\ \text{solution".} \end{array}$$

Webster's curves:—Neglecting the temperature effect, the result obtained in the previous paper to explain Webster's Graph was

$$H \times (I_n)_{\max.} = \frac{1}{2} \alpha \mu I.$$

There ( $I$ ) was the saturation value, and it was concluded that the right hand side being constant, a rectangular hyperbola was obtained. But as was also pointed out "the actual tables do not give the product  $H \times (I_n)_{\max.}$  constant. In the case of either crystal it slightly increases with the field ( $H$ ) ..... The theoretical formula we have obtained does not account for the slight increase in the value of the product  $H \times (I_n)_{\max.}$  with increasing ( $H$ ), nor does it explain the sudden drop... "

*It seems now that the cause of the discrepancy is to be looked for in the temperature effect.* In the relation

$$\frac{1}{2} \alpha \mu I = \text{Const.},$$

we must now write

$$\sigma_n \text{ for } (I_n)$$

$$\sigma_0 \left\{ 1 - \theta_0^2 f(\theta_0^2) \right\} \text{ for } I$$

$$\text{and } \mu_0 \left\{ \begin{array}{c} \text{,,} \\ \text{,,} \end{array} \right\} \text{ for } \mu$$

and we get

$$H \cdot (\sigma_n)_{\max} = \frac{1}{2} \alpha \mu_0 \sigma_0 \left\{ 1 - \theta_0^2 f(\theta_0^2) \right\}^2 \\ - \frac{1}{2} \alpha \mu_0 \sigma_0 \left\{ 1 - 2\theta_0^2 f(\theta_0^2) \right\} \quad \text{approx.}$$

From the form of the "provisional solution," we see that, we get an exact rectangular hyperbola if  $\theta_0^2 = 0$

$$\text{i. e. } \frac{h/2 A \pi^2}{v \left( e^{h\nu/hT} - 1 \right)} = 0$$

$$\text{i. e. } T = 0$$

Secondly, if  $T = 0$ ,  $\theta_0^2$  diminishes as  $\nu$  increases, — i.e. as  $H$  increases. i.e. the product  $H \times (\sigma_n)_{\max}$  should go on increasing as  $H$  increases. This is borne out by the numbers which Webster gave to us, —

CRYSTAL B			CRYSTAL A		
H	$(\sigma_n)_{\max}$	H $(\sigma_n)_{\max}$	H	$(\sigma_n)_{\max}$	H $(\sigma_n)_{\max}$
{ 8310	{ 29.7 }*	{ 246807	3640	44.4	161616
{ 7620	{ 34.5 }	{ 262890	3100	49.1	152210
5530	43	237790	2470	53.3	141642
3500	64	224000	2150	63.4	136310
2030	96.5	195895			

These tables are given in the previous paper.

\* The only exception H rises and the product falls.

## 2. Weiß experiments in (1917) [J. de Ph. s<sup>e</sup> at 7, 1917].

These led to his deducing the result

$$\frac{H+H_m}{T} = \varphi(\sigma) \text{ and independent of } T \text{ ( See next article ).}$$

Now, this result can be arrived at from the present theory thus:—

By the " provisional solution "

$\sigma$  is a function of  $\theta_0^3$

$$\text{and } \theta_0^3 = \frac{h/2A\pi^2}{v \left( e^{hv/kT} - 1 \right)}.$$

If we retain only the classical term

$$\theta_0^3 = \frac{kT/2A\pi^2}{v^3} = \frac{2kT}{\mu(H+H_m)}$$

$\therefore \sigma$  is a function of  $\left( \frac{T}{H+H_m} \right)$ .

$$\text{i. e. } \frac{H+H_m}{T} = \varphi(\sigma).$$

Now, as we shall see, the later experiments of Weiß contradict this result. This means that the Quantum form must be retained.

### [6°] Experiments of Weiß:—

In both instances, experiments were made on nickel.

1. The paper of 1917 contains the following-argument " . . . Je définirai dorenavant le champ moléculaire pas,  $H_m = - \frac{\partial u}{\partial \sigma}$ ,  $u$  étant l'énergie de l'unité de mass de la substance, et la  $T$  et  $\sigma$  des deux variables". With obvious notation

$$\begin{aligned} du &= C\sigma dT - H_m d\sigma \\ \therefore \frac{\partial C\sigma}{\partial \sigma} &= - \frac{\partial H_m}{\partial T} \quad \dots \quad (\alpha) \end{aligned}$$

Again  $dQ = C\sigma dT - (H+H_m) d\sigma$

and  $\therefore dQ/T$  is a perfect differential . . . &c.

$$\frac{1}{T} \frac{\partial C\sigma}{\partial \sigma} = - \frac{\partial}{\partial T} \left( \frac{H+H_m}{T} \right) \quad \dots \quad (\beta)$$

From (α) and (β) we get

$$\frac{\partial H}{\partial T} = \frac{H+H_m}{T}$$

$$\text{and } - \frac{\partial C\sigma}{\partial \sigma} = \frac{\partial H_m}{\partial T} = T \frac{\partial^2 H}{\partial T^2} \dots$$

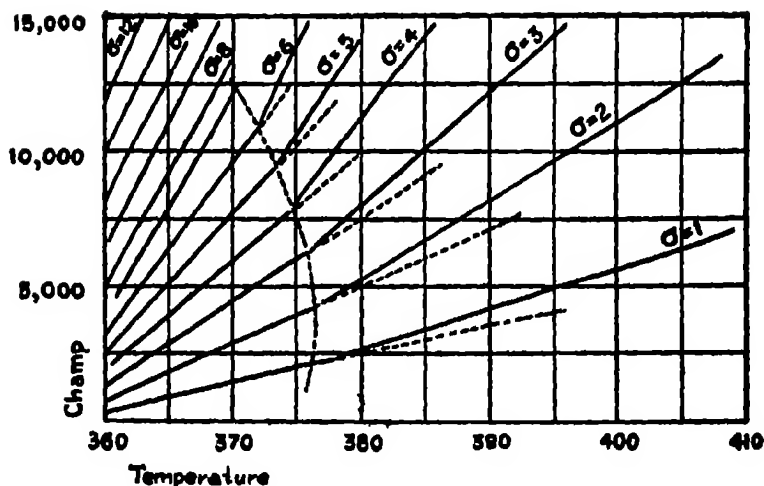
Now, the experimental curves of  $\sigma = \text{const.}$  on the  $(H, T)$  plane give straight lines

$$\therefore \frac{\partial^2 H}{\partial T^2} = 0$$

$\therefore$  We get

$$-\frac{\partial C\sigma}{\partial \sigma} = \frac{\partial H_m}{\partial T} = \frac{\partial}{\partial T} \left( \frac{H + H_m}{T} \right) = 0$$

$$\therefore \left. \begin{aligned} \frac{H + H_m}{T} &= \varphi_1(\sigma) \\ H_m &= \varphi_2(\sigma) \end{aligned} \right\}.$$



(Exact copy of "fig. 2" page 130 J. de Ph. S<sup>e</sup> 1917)

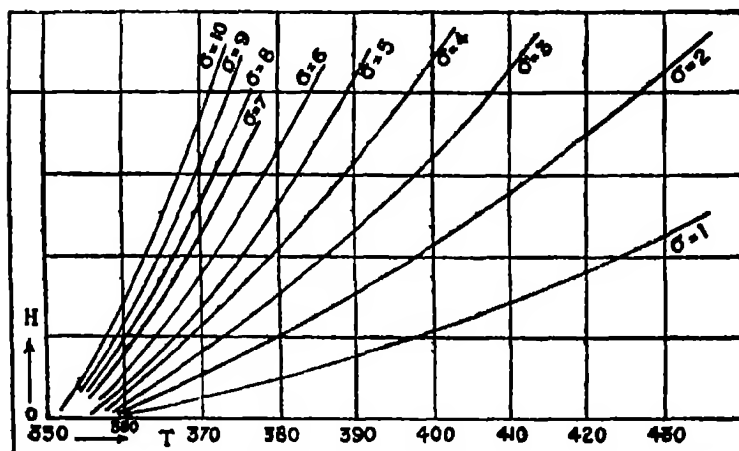
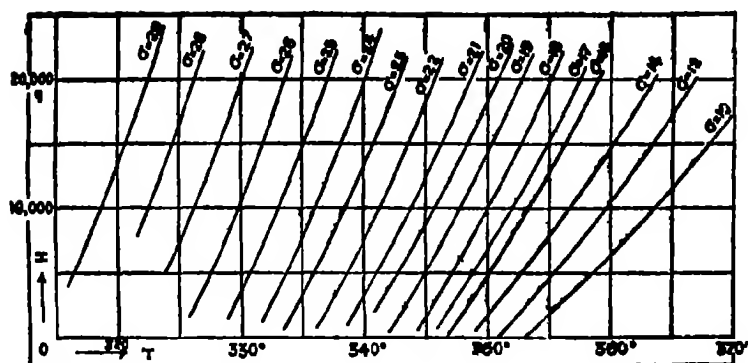
Weiß observes there, "... Mais les droites sont souvent coupées et le lieu des coudes partage le plan en régions dont chacune, il semble plausible de l'admettre correspond à un état particulier de la matière.

La relation linéaire entre la température et le champ, pour une aimantation donnée entraîne des conséquences thermodynamiques très intéressants". These 'interesting' consequences are the ones mentioned above viz.

$$(H + H_m)/T = \varphi_1(\sigma), \quad H_m = \varphi_2(\sigma).$$

2. On the other hand, the experiments in 1926 yielded curves of a different shape:— [Exact copy from Ann. de Physique Jan.-Fevr. 1926 pp. 206-7].





It is these curves, and their curvilinear character which are referred to by Weiß in the statement quoted at the very beginning of this paper. Weiß, further, observes, "Le caractère curviligne des  $\sigma = \text{constant}$ , établi au-dessus du Point de curie, n'est donc pas contredit par l'expérience au-dessous de ce point. C'est cette constatation qui oblige à modifier les hypothèses fondamentales pour l'établissement de l'équation d'état."

It will be shown now that the only 'modification' forced upon us is to accept the experimental result that

$$\frac{\partial^2 H}{\partial T^2} \neq 0$$

Notice, however, three general features about these curves.

- (i) All of them if continued down to  $T=0$  will cut the axis of  $H$  below the origin.
- (ii) The concavity in the case of all curves is away from the axis of  $T$ .

(iii) The curves tend to be straight as  $H$  increases.

These three features are borne out by the present analysis. Looking to our "provisional solution"

$$\sigma = \sigma_0 \left\{ 1 - \overline{\theta_0^2} \int (\overline{\theta_0^2}) \right\}$$

$$\text{and } \overline{\theta_0^2} = \frac{h/2A\pi^2}{v \left( e^{h\nu/kT} - 1 \right)}$$

We see that the curves  $\sigma = \text{constant}$  are given by

$$v \left( e^{h\nu/kT} - 1 \right) = \text{constant (positive)}$$

$$\text{i. e. } h\nu/kT = \log \left( 1 + \frac{\text{constant}}{v} \right)$$

Writing  $x$  for  $T$

and  $y$  for  $H + H_m$

and substituting  $(2\pi v)^2 = \mu (H + H_m)/A$

We get

$$x = \frac{L \sqrt{y}}{\log \left( 1 + \frac{M}{\sqrt{y}} \right)}$$

where  $L, M$  are positive constants.

We can write it in the form

$$\frac{x}{y} = \frac{L}{\sqrt{y} \cdot \log \left( 1 + \frac{M}{\sqrt{y}} \right)}$$

Inspection shows that

(i) the curve passes through the origin  $x=y=0$

(ii)  $\frac{x}{y}$  increase as  $y$  increases From these two facts it

follows that the concavity of the curve is away from the axis of  $x$  (i.e.  $T$ ).

Next since  $y = H + H_m$ , and since the curve passes through  $(0,0)$ , the effect of taking  $H$  only for  $y$  is to shift all the curves downwards—i.e. to say they will cut the axis  $y$  (i.e.  $H$ ) below the origin.

(iii) Observe also that the equation

$$x = \frac{L \sqrt{y}}{\log (1 + M/\sqrt{y})}$$

reduces to  $x = \frac{L}{M} y$  for large values of  $y$  i.e. the curves tend to be

straight lines as  $y$  increases. This is a characteristic which is possessed by the curves in question as given.

[7°] *General Remarks:—*

As regards testing the theory quantitatively, we have seen the difficulties, and the question is postponed for the present. In fact the so-called 'monochromatic' formula for the equation of magnetic state does not represent the reality, since we cannot neglect the coupling forces between the atoms. Besides, owing to the discovery of the difficulty about the order of magnitude,—and hence the inadequacy of the approximation,—(which discovery came too late to rewrite the whole paper)—it seemed best to adopt what we have called the "provisional solution". The defects of the provisional solution must be explicitly mentioned here —

$$\left. \begin{aligned} \bar{\mu} &= \mu \frac{1}{1/\nu} \int_0^{1/\nu} \cos \theta \, dt & \dots & (a) \\ \theta &= \theta_0 \cos 2\pi\nu t & (\beta) \\ \Lambda \theta + \mu (H + H_m) \sin \theta &= 0 & (Y) \\ \bar{\theta}_0^2 &= \frac{h/2A \pi^2}{\nu \left( e^{h\nu/kT} - 1 \right)} & (Z) \end{aligned} \right\}$$

Of this system of equation (a) and (Y) are exact and will persist in any approximation

(β) is a solution of (Y) only to approximation up to  $\theta^2$ , and in that case

$$(2\pi\nu)^2 = \mu(H + H_m) / A$$

But if this be accepted, then surely we cannot avoid accepting

$$\bar{\mu} = \mu(1 - \theta_0^2/4)$$

Since, if  $\sin \theta$  can be replaced by  $\theta$ ,  $\cos \theta$  must be capable of being replaced by  $1 - \theta^2/2$ . But that leads to an absurd result. Therefore we could not expand  $\cos \theta$  up to  $(1 - \theta^2/2)$ . And hence the relations

$$\theta = \theta_0 \cos 2\pi\nu t$$

$$\text{and } (2\pi\nu)^2 = \mu (H + H_m) / A$$

are not valid for the approximation required

And hence the provisional solution is defective,—as it is a mixture of two degrees of approximation. Yet, it is hoped that the main argument will remain unaltered, even when the exact solution is obtained

[8°] *Hysteresis —*

The concept of 'libration' gives the following picture of hysteresis.

Suppose we start from the unmagnetized state. The atomic axes are pursuing a random rotary motion (as in Langevin's theory),

or are possibly librating about several directions symmetrically situated, (as seems proper in the case of crystals), that is to say the motion is general but only a superposition of several definite frequencies determined by the crystal structure and the coupling forces. The point is that there is no privileged direction. Introduce a field  $H$ . This establishes such a direction. The general motion of 'libration at random' begins to be modified, and the atomic axes tend to librate about this direction more and more. The body thus shows a tendency to magnetization. As  $H$  increases, the frequency of libration increases, the maximum amplitude diminishes (if  $T$  is to remain the same), and consequently the average moment of the atom in the direction of the libration axis increases. This causes increase in the magnetization ( $\sigma$ ).

Now suppose the field  $H$  is removed. This removal does not change librations into random motion at once. There is the field  $H$  created in the process of magnetization. That still persists. The effect of removing  $H$  is simply to decrease the frequency, and hence to increase the amplitude (if temperature is to remain the same), and thus diminish the magnetization. If  $H_m$  is strong enough a point will be reached when  $H_m$  is sufficient to maintain the librations without further decrease in the frequency. The corresponding magnetization will remain, and the body will behave as a permanent magnet ever afterwards. *That is Hysteresis.*

If, on the other hand,  $H_m$  is not sufficiently strong, the decrease in frequency will soon bring about a state when the atoms, one after another, begin to break away from the libratory motion, to lapse into a random motion. This reduces ( $\sigma$ ), and consequently  $H_m$  also diminishes. In this way the process once started, gets accelerated, and in the later stages, the magnetization dies away quickly. This again explains the lag of ( $\sigma$ ) behind ( $H$ ). The time taken by the body to return to the unmagnetized state will of course depend upon its structure and the nature of the constituent atoms.

### [ 9° ] *Conclusion* —

1. It is suggested that the concept of temperature can be brought in the theory of Ferromagnetism by means of libration frequencies. The method requires to be fully worked out by means of a polychromatic formula. The 'monochromatic,' formula which is worked out gives absurd quantitative results, *if only the first approximation is taken.* The exact form of the solution explains *qualitatively* the results of Weiß's latest experiments. It may be that this way of introducing temperature will not answer the facts. But almost all extant theories on magnetism have been unsatisfactory. And it is as yet too early to say whether this method will or will not work.

2 The recent experiments on the specific heat of Ferromagnetic Substances do not agree with Weiß theory of the same (cf: quotation at the beginning of this paper),—it seems very likely that a satisfactory theory can be worked out on the present lines—i. e., by adopting Born's way and introducing in addition, librational frequencies.

*Note 1.*—Mckeehan's suggestion that magnetization must proceed discontinuously in space as well as in time assumes, as he himself admits that there is a slight inhomogeneity in the matter. Now we are here trying to build a working theory for a crystal. And thus the argument of inhomogeneity can scarcely hold good.

On the other hand even in the regular structure of crystals quantum processes will introduce discontinuities, due to the sudden jumps of electrons from one stationary orbit to another, the magnetic moments of atoms will suddenly change. This possibility is never denied. But it is so difficult to take account of it mathematically. In that case the only change in our statement will be:—

"Let  $\mu$ —average moment of the atom for a long time."

Again, there is no reason why the assumption of groups should be opposed to atomic processes, as far as the observable phenomena are concerned. The sub atomic process may not admit of 'groups-assumption.' But when once that is got over by putting

$\mu$ —average moment . &c ,

the groups-assumption can well be introduced, if required.

*Note 2.*—Alternative formula for the equation of state.

[1°] We shall follow LIVEN'S method, p 392 but we must take account of the following three points of difference —

(a) In LIVEN'S case the magnetic potential energy is put down as

$$-\mu B [A \phi \sin^2 \theta + C \cos \theta (\psi + \phi \cos \theta)].$$

Here each charged particle is separately considered, and on account of the gaseous state collisions are not excluded

In our case, on the other hand, our magnetic molecules (or elementary magnets) are so to say fixed at the lattice-points. Each of these is a complex structure, but is now treated as a magnet with moment  $\mu$ . The individual motions of the orbital electrons are not taken any notice of,—and hence the molecule as a whole has the magnetic energy  $-\mu H \cos \theta$ . We may suppose that our magnetic molecule is somewhat like an elongated ellipsoid of rotation.

For a Ferromagnetic molecule,  $\mu$  is fairly great to be sensibly regarded as constant.

∴ Instead of *Livens'* expression we adopt

$$- \mu H \cos \theta \text{ for the potential energy.}$$

[The justification for assuming the above model is—".. Man kann somit out eine langgerstreckte from der Elementar magnete schließen, deren länge sich aber vorerst richt abschätzen läßt. Auch sprechen diese Versuche zugunsten der Hypothese, da  $\beta$  im "magnetisch reinen Eisen" die Elementarmagnete vorgebildet sind, . . . v". Gerlach.].

(b) It is easily seen that in our case,  $E \equiv T + V$  is conserved.

(c) Thirdly, we assume that the 'ellipsoidal' magnets have no spin about their axes.

$$\text{i.e. } n \equiv \dot{\phi} + \phi \cos \theta = 0$$

[2°] Thus in our Ferromagnetic case the problem becomes

$$\left. \begin{array}{l} T = \frac{1}{2} A (\dot{\theta}^2 + \sin^2 \theta \dot{\phi}^2) \\ V = - \mu H \cos \theta \end{array} \right\}.$$

where  $H$  = total field present.

Now following *Livens* we have

$$\Theta = \frac{\partial L}{\partial \dot{\theta}} = A \dot{\theta}$$

$$\Phi = \frac{\partial L}{\partial \dot{\phi}} = A \sin^2 \theta \dot{\phi}.$$

$$\therefore E = \frac{\Theta^2}{2A} + \frac{\Phi^2}{2A \sin^2 \theta} - \mu H \cos \theta.$$

With obvious notation

$$dn = \alpha e^{-E/kT} d\Omega$$

$$d\Omega = \sin \theta d\theta d\phi d\Theta d\Phi.$$

$\alpha$  is determined from

$$n = \alpha \int e^{-E/kT} d\Omega.$$

Now obviously we get the magnetization per unit volume as

$$\sigma = \frac{n \mu \iiint \cos \theta \cdot e \left\{ \mu H \cos \theta - \frac{\Theta^2}{2A} - \frac{\Phi^2}{2A \sin^2 \theta} \right\} / kT}{\iiint \int e \left\{ \dots \right\} / kT \sin \theta \cdot d\theta \cdot d\phi d\Theta d\Phi}.$$

Now the integrations with respect to  $\phi$  and  $\Theta$  simply cancel out from the numerator and denominator, and we are left with,

$$(\because n \mu = \sigma_{\phi} \text{ saturation}).$$

$$\sigma = \sigma_0 \frac{\int \int \cos \theta \cdot e^{\left\{ \mu H \cos \theta - \frac{\Phi^2}{2 A \sin^2 \theta} \right\} / kT} \sin \theta d\theta d\Phi}{\int \int e^{\left\{ \mu H \cos \theta - \frac{\Phi^2}{2 A \sin^2 \theta} \right\} / kT} \sin \theta d\theta d\Phi}$$

[If we were to put  $\Phi=0$ , we get back to Langevin's case].

As in Langevin's case the limits for  $\theta$  may be taken as 0 to  $\pi$ .

Then putting  $x$  as  $\cos \theta$ , we get .—

$$\sigma = \sigma_0 \frac{\int_{-1}^{+1} dx \int d\Phi \left[ x e^{\left\{ \mu Hx - \frac{\Phi^2}{2A(1-x^2)} \right\} / kT} \right]}{\int_{-1}^{+1} dx \int d\Phi \left[ e^{\left\{ \mu Hx - \frac{\Phi^2}{2A(1-x^2)} \right\} / kT} \right]}$$

We take the limits for  $\Phi$  to be  $-\infty$  to  $+\infty$ . For, as

$\Phi = A \sin^2 \theta \phi$ , there is nothing geometrically impossible for  $\phi$  to be very large.

Now carrying out the integrations with respect to  $\Phi$  first, and using

$$\int_{-\infty}^{\infty} e^{-a^2 x^2} dx = \sqrt{\pi}/a, \text{ we get}$$

$$\sigma = \sigma_0 \frac{\int_{-1}^{+1} dx \cdot x e^{\mu Hx/kT} \times \sqrt{2A(1-x^2)/kT} \cdot \sqrt{\pi}}{\int_{-1}^{+1} dx \cdot e^{\mu Hx/kT} \sqrt{2A(1-x^2)/T} \sqrt{\pi}}$$

$$\text{i. e. } \sigma = \sigma_0 \frac{\int_{-1}^{+1} x \sqrt{1-x^2} e^{\mu Hx/kT} dx}{\int_{-1}^{+1} \sqrt{1-x^2} e^{\mu Hx/kT} dx}$$

Note :—This formula for Ferromagnetism differs from Langevin's for Paramagnetism in three respects :—

- (i) presence of the extra factor  $\sqrt{1-x^2}$
- (ii)  $\sigma_0 (-n\mu)$  is much greater for a Ferromagnetic substance.
- (iii) in  $e^{\mu H/kT}$ ,  $H = H \text{ external} + H \text{ internal}$ .

The internal  $H$  may be put equal to  $N\sigma$  following Weiss,—or equal to  $Nf(\sigma)$  more generally. [ $f(\sigma)$  an odd function].

It is to be noticed that the final result comes out independent of  $A$ .



## DISCONTINUOUS FLUID MOTION

By

Mr. S. D. MANERIKAR B A , (Bom. & Cantab.)

The general equations of motion of a fluid, when its viscosity and compressibility are neglected, were discovered by Lagrange and Euler. But it was found that some of the results according to this theory—the so-called classical Hydrodynamics—are in complete disagreement with observed results, even in the case of fluids like water whose viscosity is very small and was considered unimportant. So much so that practical people were doubtful as to whether there was any relation between theoretical Hydrodynamics, and the actual behaviour of fluids.

Some of these surprising results may be mentioned. According to this theory, a body exposed to a stream of perfect fluid would experience no resultant force at all, any pressure on its face being compensated by equal and opposite pressure on its rear. A particular case of this viz. when the body is a sphere was first solved by Dirichlet and is known as "Dirichlet's paradox."

According to the classical theory the form of flow about a symmetrical body is the same behind as in front. This is quite different from what is observed in actual practice. If a flat plate is held fixed in moving water, the liquid refuses to close in behind, and a region of more or less "dead-water" (i.e. still water) is formed, entailing a large resistance.

Thirdly, according to theory, the velocity of the fluid at the sharp edge of an obstacle should become infinite. In practice the velocity is very great to start with, but speedily diminishes owing to the formation of an eddy.

Fourthly, the classical theory would involve negative pressure in a fluid. Rayleigh remarks that there is nothing in the constitution of a perfect liquid to prevent the existence of negative pressure. But in actual practice it is not observed in the cases, where according to the classical theory it should occur.

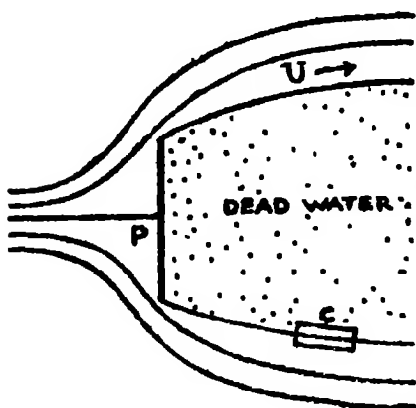
It is clear therefore that some alteration is necessary. If we take viscosity into account, the problem becomes too hard. No general solution of the equations for a viscous fluid has yet been given, though particular cases have been solved. The scientist therefore still kept the assumption of a perfect liquid.

It was Helmholtz who first pointed out that there was nothing in the nature of a perfect fluid to forbid a finite slipping between con-

tiguous layers and that the possibility of such an occurrence was not taken into account in the common theory.

To make clear the improvement effected by this theory let us consider the case of a flat plate moving in still water. This was solved by Kirchhoff and discussed

FIG. 1.



more fully by Rayleigh (Two dimensional motion).

The fluid behind the plate is supposed to move strictly with the advancing plate and to be separated from the main fluid by a surface of separation. The tangential velocities on the two sides of the surface are different. There is no velocity normal to the surface.

If the plate be assumed fixed and the fluid to flow about it, the fluid behind the plate

is at rest under a pressure equal to that which prevails at a distance. The surface of discontinuity is determined mathematically by condition of constant pressure (equal to the pressure in the "dead-water" region).

If  $p$  is the pressure and  $u$  the velocity at a distance, and  $\rho$  the density of fluid, the pressure at the middle-point of the front side of the plate is by Bernoulli's equation  $p + \frac{1}{2}\rho u^2$  (since at this point the liquid comes to rest). The pressure on the rear side is  $p$ . If the liquid were to come to rest at all points on the front side, we should get the total resistance equal to

$$\frac{1}{2} \rho u^2 \times \text{the area of the plate.}$$

This is only an approximation. The liquid does not come to rest at all points of the plate, and more exact theory gives the total resistance equal to

$$\frac{\pi}{4 + \pi} \rho u^2 \times \text{the area of the plate.}$$

$$\left( \frac{\pi}{4 + \pi} = 0.44 \text{ approx.} \right)$$

Experimentally, the resistance is found to be about  $\rho u^2 \times$  area of the plate, i. e. more than twice as great as the theoretical value.

The reason for this disagreement between the theoretical and the experimental values is this. In practice the pressure just behind the plate is not equal to, but less than  $p$  the pressure at a distance. This cannot be taken into account in Kirchhoff's theory.

But the new theory is a great improvement on the older one, which did not give any resistance at all. At the edges the new theory does not give infinite velocity. It does not give rise to negative pressures, and the form of the flow according to this theory agrees better with experiment than the form of flow according to the older theory did.

Let us now consider some of the objections that have been raised against this theory. Lord Kelvin objected that the motion was contrary to the "minimum energy theorem" (called after him). As Lanchester points out this objection has no force. For the minimum energy theorem assumes the absence of discontinuity, and when the assumption is rejected, Kelvin's theorem does not hold.

A second objection put forward by Kelvin was that such a surface of discontinuity would be unstable. This objection is perfectly valid and explains why in practice such a surface is not observed. There is no sharp dividing line between the main flow and the "dead water" region.

A third objection is the existence of circulation along the rectangular curve C (see figure 1). By Kelvin's theorem circulation along a closed curve moving with the fluid (assumed incompressible and non-viscous) does not change. As there was no circulation at a distance in front of the plate, it is argued that it is not possible to have circulation behind. On the other side it is argued that this circulation is due to viscosity, and that though in an inviscid fluid, the circulation could not occur, the objection does not hold for a fluid with small viscosity. The argument is incorrect. For though it is possible to generate circulation in the viscous fluid, yet *quantitatively* the existence of so much circulation in a fluid with negligible viscosity cannot be explained.

The error in the objection was discovered very late. Kelvin's theorem applies to curves moving with the fluid. The curve C has not moved with the fluid. The lower portion has come with the main portion of the fluid, while the upper portion has always been there. Hence before some time the particles forming the upper and the lower portions respectively were separate, and the two together did not form a closed curve.

It has been mentioned that the theoretical form of flow does not agree well with the observed. It is assumed in the theory that with respect to a co-ordinate system moving with the body, the flow is stationary, which is certainly not true.

According to the theory there is no "suction" behind the body, because in the dead-water region the pressure is constant and equal to the pressure at a great distance from the body. But experiment shows that this suction has a great influence on the resistance experienced by the body.

The reason why the hydrodynamically possible discontinuous potential flow does not exist, lies in the instability of the surface of discontinuity. (See above)

One can think of the surface of discontinuity as a "vortex-layer." This vortex-layer shows a tendency to "curl," i. e. the vorticity is concentrated at some points and taken away from the region between these points. This observation suggests that there may be stable arrangements of isolated vortices, which can be regarded as the end-product of the vortex-layer.

Such an arrangement was found by Kármán, called Kármán vortex-street after him. By assuming the existence of such an arrangement behind the body Kármán calculated the resistance on a cylinder (two-dimensional flow). He found it equal to  $\rho \zeta \frac{h}{l} (U - 2u)$

+  $\rho \frac{\zeta^2}{2\pi l}$  where  $\rho$  is the density of the fluid,  $\zeta$  the vortex strength,  $U$  the velocity of the body relative to the fluid,  $u$  the velocity with which the vortex-system moves forward relative to the fluid,  $h$  is the distance between the two rows, and  $l$  the distance between two adjacent vortices of the same sign (see Lamb, p. 211 for a fig. of the stable arrangement). The calculated resistance agrees very well with the observed.

The stability consideration gives

$$\cosh \frac{h\pi}{l} = \sqrt{2} \text{ i. e. } \sinh \frac{h\pi}{l} = 1$$

$$\text{i. e. } \frac{h}{l} = 0.281 \text{ approx.}$$

$$u = \frac{\zeta}{2l} \tanh \frac{\pi h}{l}$$

Hence two of the quantities have to be determined by experiment,  $u$  and  $l$  say. In this respect Kármán's theory is not complete, for when the size and shape of the cylinder and the velocity of the cylinder relative to the fluid, are given, it is not possible to calculate the resistance without measuring two quantities.

Heisenberg (Physik. Zeit. 1922) has tried to obtain the resistance on a flat plate moving normally through a fluid. He assumes that the flow is a discontinuous potential flow to start with, but later degenerates into a Kármán vortex-street, whose dimensions he has found out from purely theoretical considerations. The results agree well with experiment. It remains now to see how the surface of discontinuity resolves itself into the stable arrangement of the Kármán vortex-street. This problem has not been solved. But Rosenhead (in P.R.S. 1928) has proved that a plane surface of discontinuity degenerates into a row of periodically distributed vortices of the same sign.

**Summary**—We have seen how the continuous potential flow did not agree well with experiment. It was modified by Helmholtz who assumed that a surface of discontinuity could occur. We have seen the objection to this, firstly that the surface is unstable, and secondly, the resistance given by it is much less than the experimental value. We have seen that Kármán and Heisenberg have found theoretical values which agree very well with experiment, and lastly we have a proof by Rosenhead that a surface of discontinuity does actually resolve into a vortex-row.

#### APPENDIX

Reference has been made to papers by Kármán and Heisenberg. A more detailed description of the two papers will be given here.

Kármán—"Über den Mechanismus des Flüssigkeits- und Luftwiderstandes". (Physik. Zs. 1912)

If we assume that at some distance behind the body the flow does not differ appreciably from the flow due to the stable vortex arrangement, and that at some distance in front of the body (the distance is large compared to the linear dimensions of the body), the fluid is at rest, then we obtain an expression for the resistance by the application of the Impulse Theorem.

We use the co-ordinate system which moves with the vortex system (which moves forward with velocity  $u = \frac{\zeta}{2l} \tanh \frac{\pi h}{l}$  with respect to the fluid at rest,  $\zeta \equiv$  Vortex strength). With respect to this co-ordinate system, on the assumptions we have made, the flow is stationary at some distance in front as well as behind the body. In front there is uniform flow with velocity  $-u$ , behind the body the velocity components are  $-u + \frac{\partial \Psi}{\partial y}$  and  $-\frac{\partial \Psi}{\partial x}$  where

$$\chi \equiv \phi + i\Psi = \frac{i\zeta}{2\pi} \log \frac{\sin(s^0 + z)\frac{\pi}{l}}{\sin(s^0 - z)\frac{\pi}{l}} \quad \left( \text{where } s^0 \equiv \frac{l}{4} + \frac{hi}{2} \right)$$

$\chi$  is due to the vortex system at rest. (See Lamb.)

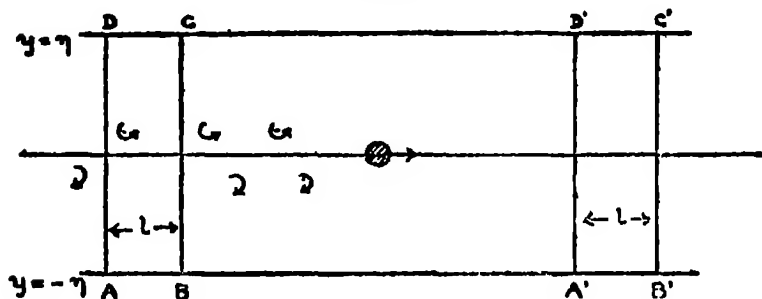
Relative to our co-ordinate system, the body moves with velocity  $U-u$ , where  $U$  is its actual velocity. In time  $T = \frac{l}{U-u}$  ( $l$  is the distance between two consecutive vortices of the same sign) a new pair of vortices is formed. We calculate the increase of  $x$ -impulse in this time  $T$  (i. e. between two instants of time after which the flow pattern is exactly the same as before) in the following region:—We take two parallels  $y = \pm \eta$ , and two parallels  $x = \text{const.}$  in front and behind the body at a great distance from the body. The line behind the body

is so chosen that it is exactly in the middle of two vortices of opposite sign.

For a region so chosen the impulse exerted on the body  $\int_0^T W dt$  (where  $W$  is the resistance) is equal to [the difference of impulse in the region at time  $t = \tau$  and  $t = \tau + T$ ] - [the impulse imported from outside] + [the time integral of the pressure on the boundaries of the region].

We shall calculate the quantities one by one. The increase in impulse in time  $T =$  increase in  $\iint \rho u(x, y) dx dy$ . But the interval

FIG. 2



$T$  is so chosen that the flow pattern reproduces itself exactly with the exception that the body has moved forward  $l = (U - u) \cdot T$ .

The whole double integral reduces to the difference of the integrals on the regions  $ABCD$  and  $A'B'C'D'$ , both of breadth  $l$ .

For  $A'B'C'D'$ , the  $x$ -component of the velocity is  $-u$ , and for

$ABCD$  it is  $-u + \frac{d\psi}{dy}$

$$\therefore \text{The whole quantity } I_1 = \rho \int_0^l \int_{-\eta}^{\eta} \frac{d\psi}{dy} dx dy.$$

If we take limit  $\eta \rightarrow \infty$ , then we obtain

$$I_1 = \rho \zeta h.$$

The sum of the imported impulse and the time integral of pressure will be taken together.

If we take any potential flow  $u(x, y)$ ,  $v(x, y)$  and consider a certain region, then the  $x$ -impulse imported per sec  $= \rho \int (\bar{u}^2 dy - \bar{u} \bar{v} dx)$ , where  $\bar{u}$ ,  $\bar{v}$  are the velocity components on the boundary. The pres-

sure gives, for  $x$ -component,  $\int \bar{p} \, dy$ . By Bernoulli, in stationary potential flow  $\bar{p} = \text{const} - \rho \frac{\bar{u}^2 + \bar{v}^2}{2} \therefore$  The sum of both integrals (multiplied by time  $T$ ) is

$$\begin{aligned} I_2 &= T \left\{ \int \rho (\bar{u}^2 \, dy - \bar{u} \bar{v} \, dx) + \int \bar{p} \, dy \right\} \\ &= T \rho \int \left[ \frac{\bar{u}^2 - \bar{v}^2}{2} \, dy - \bar{u} \bar{v} \, dx \right] \end{aligned}$$

or if we introduce  $\bar{w} = \bar{u} - i\bar{v} = \frac{\partial \chi}{\partial z}$

$$I_2 = \frac{Tp}{2} \text{Im} \left( \int \bar{w}^2 \, dz \right)$$

where  $\text{Im}$  denotes that the imaginary part is to be taken.

On the boundaries we put  $\bar{u} = -u + u'$ ,  $\bar{v} = v'$  then the terms in  $u^2$  disappear; the terms in  $u$  also disappear by continuity (the incoming fluid = the outgoing fluid), and only the terms in  $u'^2$ ,  $u' v'$  remain. This gives a value on the line which goes through the vortex-system (AD in fig.).

If we let  $\eta \rightarrow \infty$ , then

$$\begin{aligned} I_2 &= \frac{Tp}{2} \text{Im} \left\{ \int_{-\infty}^{\infty} \left( \frac{\partial \chi}{\partial z} \right)^2 dz \right\} \text{ along AD} \\ &= \frac{Tp}{2} \text{Im} \left\{ \int_{\chi(-\infty)}^{\chi(\infty)} \frac{\partial \chi}{\partial z} d\chi \right\} \text{ along AD} \\ &= Tp \left\{ \frac{\zeta_u h}{l} - \frac{\zeta^2}{2\pi l} \right\} \end{aligned}$$

$$\therefore \int_0^T W dt = \rho \zeta h - Tp \left( \frac{\zeta_u h}{l} - \frac{\zeta^2}{2\pi l} \right)$$

If we put  $\bar{w}$  instead of  $\frac{1}{T} \int_0^T w \, dt$ , then since  $T = \frac{l}{U-u}$

$$\bar{w} = \rho \zeta \frac{h}{l} (U - 2u) + \rho \frac{\zeta^2}{2\pi l}$$

W. Heisenberg "Dimensions of the Karman Vortex-motion"

Figure 1 (already given) represents the flow (2-dimensional) about a plate of length  $d$  (Kirchhoff's discontinuity flow). It is the only known flow for which the velocity at the end of the plate remains finite. The shaded portion behind represents the "dead-water", and the lines bounding the portion the curves of discontinuity.

These curves are known to be unstable. We assume that very near the plate the curves of discontinuity exist, and that they break up at some distance behind. This assumption is justified on experimental grounds.

Let  $U$  be the velocity of the plate relative to the water (assumed to be at rest at  $\infty$ ) and let  $u$  be the velocity of the vortices. Then relative to the vortices, the velocity of the plate is  $U - u$ . Let  $l$  be the distance between two successive vortices of the same sign. Then  $T = \frac{l}{U - u}$  is the period, or the time between the shedding of two successive vortices of the same sign. If  $\zeta$  is the strength of each vortex, then if we consider the upper row of the "Karman vortex-street" only (assumed to arise from the breaking up of the upper surface of discontinuity)  $\zeta$  is the increase of circulation in time  $T$  or  $\zeta/T$  per unit time  $= \frac{\zeta}{l} (U - u)$  . . . . . (1)

In the dead-water the velocity is zero. Outside the velocity is  $U$ .

$\therefore$  The curve of discontinuity itself moves with velocity  $\frac{U}{2}$ .

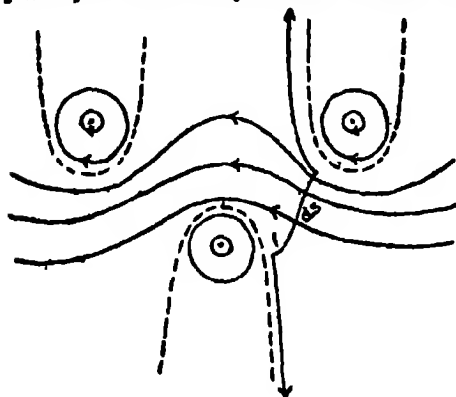
$\therefore$  Length of curve generated per unit time  $= \frac{U}{2}$  . . . . . (2)

$\therefore$  Circulation generated per unit time  $= U \frac{U}{2}$  . . . . . (2)

Since in an incompressible frictionless fluid the circulation remains unaltered, the two expressions (1) and (2) must be equal.

$$\therefore \text{e.}, \frac{U^2}{2} = \frac{\zeta}{l} (U - u) . . . . . (3)$$

Another equation is obtained from the fact that a certain fixed quantity of water always moves forward between the two vortex rows.



(Outside the vortex rows a particle does not move very far from its original place. But inside, it is continually moving.)

This quantity of water  $\equiv$  the water pushed forward by the plate  $= U \cdot d$ .

According to Karman the complex potential of the "vortex street" is



$$\chi = \frac{i\zeta}{2\pi} \log \frac{\sin(s^0 - s) \frac{\pi}{l}}{\sin(s^0 + s) \frac{\pi}{l}} \quad \dots \dots \dots (4)$$

$$\text{where } s^0 = \frac{l}{4} + \frac{hs}{2}$$

$$Q \text{ the quantity of water} = \int_a^b U_n ds = \int_a^b I(W ds)$$

where  $I \equiv$  imaginary part and  $W = u - iv = \frac{d\chi}{ds}$

$$\therefore Q = I \int_a^b \frac{d\chi}{ds} ds = I \int_a^b d\chi = [I(\chi)]_a^b$$

The termini  $a, b$  of the integral must lie on the stream lines—the boundaries of the required water flow. The exact position of  $a, b$  on the stream-lines does not matter. In the present case, the boundary stream-lines are the only ones which  $\rightarrow \infty$  in the  $Y$  directions.  $\therefore a = -i\infty, b = +i\infty$  may be chosen. The path of integration is from  $s = -i\infty$  along the stream line till we come near the vortex, then along  $ds$ , and then along the other boundary stream line to

$$s = +i\infty \quad \therefore \quad Q = I(\chi_{+i\infty} - \chi_{-i\infty})$$

Now by (4)

$$\chi_{a+\beta i} = \frac{i\zeta}{2\pi} \log e^{\frac{i\pi}{l}(\frac{l}{4} + \frac{hs}{2} - a - \beta i)} - \frac{i\pi}{l}(\frac{l}{4} + \frac{hs}{2} - a - \beta i) \\ e^{\frac{i\pi}{l}(\frac{l}{4} + \frac{hs}{2} + a + \beta i)} - \frac{i\pi}{l}(\frac{l}{4} + \frac{hs}{2} + a + \beta i)$$

For  $\beta \rightarrow \infty, a = 0$  ( $a$  does not appear in the imaginary part of  $\chi$ ).

$$\chi_{+i\infty} = \frac{i\zeta}{2\pi} \log \left( -e^{\frac{i\pi}{2} - \frac{h\pi}{l}} \right) = -\frac{3\zeta}{4} - \frac{i\zeta h}{2l}$$

$$\chi_{-i\infty} = \frac{i\zeta}{2\pi} \log \left( -e^{-\frac{i\pi}{2} + \frac{h\pi}{l}} \right) = -\frac{\zeta}{4} + \frac{i\zeta h}{2l}$$

$$\text{Hence } |I(\chi_{+i\infty}) - I(\chi_{-i\infty})| = \frac{\zeta h}{l} \quad \dots \dots \dots (5)$$

$$\therefore Ud = Q = \frac{\zeta h}{l} \quad \dots \dots \dots (6)$$

$$\text{Karman gives } \frac{\zeta}{l\sqrt{g}} = 1u \quad \dots \dots \dots (7)$$

$$\frac{h}{l} = 0.281 \quad \dots \dots \dots (8)$$

From (3)  $\frac{1}{2} U^2 = u\sqrt{g}(U-u)$ .

$$i. e. 1 = 2\sqrt{8} \frac{u}{U} \left(1 - \frac{u}{U}\right)$$

gives  $\frac{u}{U} = 0.229 \dots \dots \dots (9)$

or  $\frac{u}{V} = 0.771 \dots \dots \dots (9a)$

From (6), using (7) and (8).

$$Ud = u \sqrt{g \cdot l \cdot (0.281)}.$$

using (9)  $\frac{I}{d} = \frac{1}{\sqrt{8} (0.281) (0.229)} = 5.45 \dots\dots (10)$

$$\frac{h}{d} = 1.54 \quad . \quad . \quad . \quad . \quad . \quad (11)$$

(9a) gives a much smaller value for  $\frac{l}{d}$  and  $\frac{h}{d}$ , but as the curves of discontinuity are inclined outwards this possibility cannot be realised. Kármán gives as empirical values

$$\frac{16}{U} = 0.20, \quad \frac{l}{d} = 55$$

The resistance also agrees well with experiment

## \* RELATIVITY AND COSMOLOGY—PART I

*By*

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### INTRODUCTION

I should like, in the very first instance, to express my most sincere thanks to the University of Bombay for their kind invitation to give this course of lectures. I am alive to the honour they have done me thereby and incidentally to the responsibility that rests on my shoulders in return.

I did not want to lecture on relativity alone as the subject has of late gone into a rut. Moreover it has lost, in a relative sense, the glamour it had during the first few years after the war. On the other hand the subject of cosmology is centuries old. Men in almost every walk of life, philosophers of almost every shade of opinion have indulged in the very fascinating game of speculating on the origin of the universe. Cosmology is, therefore, a vast subject and I know nothing of its extension in the strictly philosophical domain. I have therefore decided to give a short account of certain principles of relativity that would facilitate a smooth entry into the domain of cosmology.

The relativistic treatment of cosmology is fascinating from the stand-point of sheer mathematics. It has a number of problems that look as if they can be easily solved and yet have defied the attacks of some of the most eminent mathematicians, past and present. It is an excellent field for the research students who are hunting after problems and I have therefore chosen this for my subject.

The Theory of relativity can be studied from four different points of view. (1) Gravitational astronomy, (2) Geometry, (3) Electrodynamics, and (4) Philosophy.

Let us now consider how the need for the theory of relativity arose from the standpoint of gravitational astronomy.

The three laws of Kepler concerning the motions of the major planets about the sun are very well-known. Newton deduced from them the law of gravitation which has achieved such remarkable success not only in the solar system but in all the regions of space that have been so far explored. According to the first law of Kepler each planet

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\*This is a report of six lectures delivered on the subject in January 1933 by Prof. V. V. Narlikar under the auspices of the University of Bombay.

moves in an ellipse of which a focus is at the sun. The second says that the radius vector from the sun to the planet describes equal areas in equal intervals of time, while the third is that the square of the periodic time varies as the cube of the mean distance. It is true that the planets move in a rough sort of way so as to be subject to these laws. But if we take the Newtonian law of gravitation as fundamental and Kepler's empirical laws as the consequences of the former then the motion of any planet is perturbed owing to the gravitational attraction of the other planets in the solar system. Thus Newcomb<sup>1</sup> has shown that one result of perturbation in the case of the Mercury is that the ellipse of Mercury itself rotates about the sun at the rate of  $532''$  per century. But it has been observed that the rotation is approximately  $575''$  a century i. e.,  $43''$  per century more. On the Newtonian hypothesis no satisfactory explanation of this extra rotation could be given. Several attempts were made to account for these extra  $43''$  per century but to no success and it was ultimately left to the theory of relativity to explain the phenomenon. We will come to these considerations later on but it ought to be remarked here that the success of the theory of relativity in this particular is attributed more to chance than to any intrinsic merit in the latter.

An interesting position presents itself at this point. Kepler's objection to the geocentric theory of the universe in which the planets moved in cycles and epicycles was that it could not account for some  $8'$  in the revolution of Mars. Thus the Newtonian theory arises out of the  $8'$  of Mars while Einstein's theory arises out of the  $43''$  of Mercury. One expects that an improvement on Einstein could emanate only out of a still more subtle phenomenon.

Next consider the approach to relativity from the geometrical point of view. Before the advent of the theory of relativity it was customary to use Euclidean geometry for the exploration of all the fields of physics. That the parallels meet at infinity, which is an axiom of Euclidean Geometry is certainly contrary to common experience; and it has therefore to be taught at school as that ultimately, it becomes assimilated into one's habit of thought. As it is beyond the scope of our observation we may with equal justification say that parallels meet at any distance of the order of  $10^{10}$  miles. If therefore our space is not subject to the Euclidean geometry the possibility arises that the empirical laws of physics which hold good in our neighbourhood may not do so for the large-scale phenomena. Now cosmology is concerned with such large-scale phenomena and it is therefore necessary to apply non-Euclidean geometry to the study of the physics of cosmology. Thus relativity and cosmology can be studied even from the geometrical point of view.

Maxwell's equations for electromagnetic phenomena are true only for a fixed frame of reference. The form of these equations when

referred to a uniformly moving set of axes was first given by Lorentz. But Lorentz's form demanded a distortion in the space-time frame which appeared absurd on the basis of classical ideas. Lorentz and others contended that this distortion was due to the drag of the all-pervading ether on the moving frame and that the distorted space and time were not, therefore, real. The classical conception of the ether was, however, soon found to be unsatisfactory and relativity came forward which, while it retained the mathematical analysis supplied by Lorentz gave a strikingly new interpretation to the mathematical results. The details, we may for the present leave aside as our business now is only to indicate how a topic in electromagnetism leads to the theory of relativity.

It becomes obvious from Einstein's earlier papers on the theory of relativity that a good deal of his inspiration came from the philosopher Mach.<sup>2</sup> The latter questions the very soundness of the ideas of space and time which Newton expresses in "The Principia". In his "*Principles of Mechanics*," published in 1893, Mach<sup>3</sup> argues that it is a very idle suggestion of Newton's that the time flows on uniformly. The flow can be uniform only with reference to something and hence the phrase, "uniformity of flow" has got no meaning in the absence of a standard. The conception of time probably arose out of a necessity. Our forefathers perhaps found it necessary to regulate their lives some way in which case it seems reasonable to suppose that the rising and setting of the sun provided them with a standard to mark off equal intervals. Thus the classical theory of space and time did not satisfy some of the searching philosophers of the pre-relativity days and a new theory such as the relativity theory was hunted for.

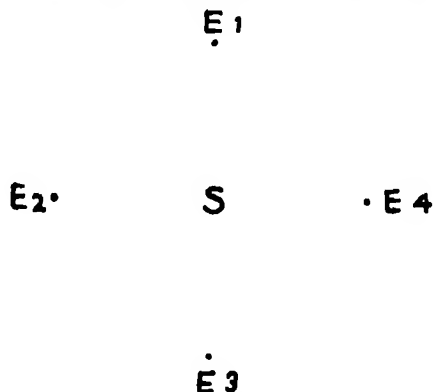
The modern conception of the universe is that it is a finite and unbounded hypersphere of radius  $10^{27}$  cms., approximately. Yes! It is at once finite and unbounded in the same sense that a circle has a finite length but neither any beginning nor an end. The total mass in the universe is estimated at about  $10^{55}$ , the mass of the sun being  $1.99 \times 10^{33}$  grs. Incidentally it becomes obvious that even as regards its mass the sun is a mere nobody in the galaxies of the universe, and the question arises as to how all the masses in the universe are distributed in space.

It has been estimated that there are over  $10^{10}$  stars in the universe. All these stars, planets, nebulae, and other celestial bodies seem to possess each some relative motion with reference to the other bodies in the universe. There seems to be no body in the sky which is at absolute rest. The Greeks thought that the Earth is at rest and that all the other bodies in the space move about the earth. It was left to Kepler, as we have already remarked to pull this theory to pieces. It should however be observed that even if the geocentric theory of the universe was disproved by Kepler he had not yet proved that the

earth cannot be at absolute rest. The question was still open to enquiry and experiments were proposed from 1887 onwards to determine the absolute motion of the earth. It was quite in keeping with the philosophy of the time to imagine that some sort of a fixed medium, no matter how rare, extends over the whole space, in which all the material bodies are suspended. Such a medium may have fixed landmarks with reference to which they thought of measuring the velocity of the earth.

It is needless to go here into the series of experiments which are associated with the name of Michelson. Suffice it to say that the central question of the absolute motion of the earth slipped through the search of all experimenters. One important outcome of all the experimental investigations was that it was found out that the velocity of light cannot be compounded with the velocity of the source according to the parallelogram law. That this is so has been very ingeniously propounded by de Sitter from certain considerations of double stars. To make the argument simple we will treat the system of the sun and the earth as a double star

In the accompanying diagram  $S$  is the sun and  $E_1, E_2, E_3$  and  $E_4$  are four positions in the orbit of the earth such that the time to pass from any one position to the next is three months. According to the classical ideas if  $v$  is the velocity of the earth in the orbit and  $c$  the velocity of light, the latter will leave



$E_1$  in the direction  $SE_4$  with velocity  $c-v$  and six months later light will leave  $E_3$  in the direction  $SE_4$  with velocity  $c+v$ . Thus the light from  $E_3$  moves with a greater velocity than the light from  $E_1$  and it is obvious that at some distance  $d$  an observer will receive the light from  $E_1$  and  $E_3$  simultaneously. An observer so situated will see the earth simultaneously in the two positions. From a simple calculation one can see that such an observer will have to be about  $10^{16}$  kms., from the sun. Now about thirty to forty per cent of the stars in any cluster are generally double stars and an occurrence as anticipated by de Sitter should be a matter of common observation. But as this phenomenon has not been observed one expects that the classical law of the composition of velocities fails when one of the velocities concerned is that of light.

Einstein gave quite a sensational interpretation to the failure of all experimental investigations to determine the absolute motion of the

earth. It is that it is not possible to determine the absolute motion by any optical instrument and that the velocity of light is always the same whatever be the motion of the source. The whole structure of the theory of relativity is based on this interpretation and any evidence to the contrary would be enough to destroy the relativistic philosophy. It will perhaps be of some interest to remark that Einstein's interpretation was subject to much criticism when first made and Prof. Miller<sup>4</sup> of America, one of his early critics still persists in his opposition. We find, however, hardly any sound justification for this opposition in Miller's investigations.

Einstein, therefore, enunciated as a law of nature that the velocity of light is a constant  $c$ , the same for all observers moving in any manner. A recent estimate gives  $c$  equal to  $2.99794 \times 10^{10}$  cms., sec<sup>-1</sup>. The question that now presents itself is whether any physical bodies in the universe can attain velocity greater than that of light. According to relativity a velocity greater than  $c$ , cannot be associated with matter or energy in any form as such velocities do not come within the range of experience. Many would challenge this statement as experiments could easily be suggested where a velocity greater than  $c$  should be discernible according to the classical ideas. Consider for example an experiment suggested by Eddington. If a powerful search-light, thrown from the earth, is made to rotate about eleven times a second in the plane of the orbit of Neptune then the observers at Neptune should find that the velocity of the beam as it passes across Neptune is greater than that of light. The solution which the relativist suggests to this difficulty is that the prediction of the observers of the earth as to what will be observed on Neptune is, based on the Newtonian conception of space and time. But the relativistic four-fold of space-time is warped, the time-scale near the earth is not the same as the time-scale near Neptune and it could be possible that the observers of Neptune will find the beam moving with a velocity less than  $c$ . That this is not only possible but is invariably so will be understood when an insight into the general theory of relativity is gained.

### *The Special Theory of Relativity.*

Although it is true that we are concerned only with the space and time intervals between two events, frames of co-ordinate axes facilitate the work of ordering the experiences. A rectangular cartesian frame ( $xyzt$ ) is said to be Galilean when Newton's first law holds good in that frame. Now this law states that "every body perseveres in its state of rest or uniform motion in a straight line, except in so far as it is compelled to change that state by unpressed forces". Hence if a frame  $K$  is Galilean another rectangular frame ( $x' y' z' t'$ ) which moves away from or towards  $K$  with a uniform speed in the same straight line

is also Galilean. Let us call this other Galilean frame  $K^1$ . As we have already remarked it has not been possible yet to detect the absolute motion of any body in space. Hence there is no standard Galilean frame  $K$  with reference to which only the laws of Nature need be true. In other words the laws of Nature should hold good with reference to both  $K$  and  $K^1$ , the latter being any two Galilean frames. In essence this is the principle of the special theory of relativity.

Following Einstein one expects that the velocity of light is the same whether the observer is at  $K$  or  $K^1$ . The Galilean transformation connecting  $K$  and  $K^1$  is  $x' = x - ut'$ ,  $y' = y$ ,  $z' = z$ ,  $t' = t$  when  $K^1$  moves with a uniform velocity  $u$ , along  $ox$ , and away from  $K$ . Hence if a light signal is sent along the  $x$ -axis in  $K$  the velocity of light in the latter frame would be  $c$  while it would be  $c - u$  in the other. Evidently the Galilean transformation is not consistent with the restricted principle of relativity, and a new transformation must be devised to meet the requirements.

The Lorentz transformation was found to fit in satisfactorily with the special theory. It runs as  $x' = B(x - ut)$ ,  $y' = y$ ,

$z' = z$ ,  $t' = B(t - \frac{ux}{c^2})$  where  $B = (1 - \frac{u^2}{c^2})^{-\frac{1}{2}}$ — This gives

$$dx'/dt = \frac{dx/dt - u}{1 - \frac{u}{c} \frac{dx}{dt}} \quad 2$$

so that when  $\frac{dx}{dt} = c$ ,  $\frac{dx'}{dt'}$  is also  $c$ , and conversely.

According to Lorentz who discovered the transformation in connection with electro dynamics ( $x'$ ,  $y'$ ,  $z'$ ,  $t'$ ) are not real if the other co-ordinates are. On the other hand, as there is no standard by which  $K$  can be judged to be superior to  $K^1$  Einstein puts both the frames on equal footing. This would mean drastic changes in our habits of thought about space and time.

Einstein has also deduced the Lorentz transformation from a certain set of plausible assumptions. He does this in three steps. At the very outset he assumes that the required transformation between  $(x, y, z, t)$  and  $(x', y', z', t')$  must be linear and the cause of the linearity according to him is the homogeneity of space and time. This argument has appeared obscure to some and attempts have been made to obtain the linearity from first principles.<sup>5</sup> Once the linearity is accepted Einstein next applies in succession the principles of the relativity of the rod and the clock and deduces the Lorentz transformation. The principle of the relativity of the rod is something of the following sort. A and B are two neighbours so that naturally, either discounts the other's story. A has a cow which, he says, gives eight seers of milk per day, and B thinks that the cow must be giving only four seers in place of eight. Suppose by some chance the cow becomes



the property of B. Then if B tells that the cow gives ten seers a day, A is bound to think according to the analogue of the principle in question, that the cow really gives five seers of milk in place of ten. Thus the principle of the relativity of the rod says that if a metre rod in the frame K appears to be one-tenth less in the frame  $K^1$  then a similar impression will be received in K if a metre rod is placed in the frame  $K^1$ . To understand the principle of the relativity of the clock it is necessary to know first what is meant by a clock. The function of a clock is to give equal intervals of time. Hence to get a clock ready we have only to procure a metre rod and define as a unit interval the time taken by light to traverse the distance. From the standpoint of a common observer the metre rods in K and  $K^1$  differ while the velocity of light is the same. Hence the standard clocks in K and  $K^1$  also differ. As the principle of the relativity of the rod has already been used all that the principle of the relativity of the clock amounts to is that the velocity of light is the same in both K and  $K^1$ . This is the third step in Einstein's deduction of the Lorentz transformation.

The obvious interconnection between space and time in the Lorentz transformation gives rise to quite a new philosophy. Let us consider two observers K and  $K^1$  carrying each his own Galilean frame. Suppose that the two are together at  $t = 0$  when a light signal is sent. After a time  $t$  it will lie somewhere on a sphere with centre  $o$  and radius  $ct$ , where  $c$  is the velocity of light. Let in the meantime  $K^1$ , who has a uniform velocity  $u$  along  $ox$  arrive at  $O'$  so that  $OO' = ut$ . Draw  $O'P$  perpendicular to  $OO'$  so as to meet the sphere somewhere in P. Let us suppose that the signal was originally sent in the direction  $OP$ . Let the time of reaching at P be  $t'$  according to  $O'$ . Of course  $t$  cannot be equal to  $t'$  as the measures of time of K and  $K^1$  differ. Hence  $O'P = ct'$ . The distance  $O'P$  being perpendicular to the direction of relative motion will be the same according to the estimates of K as well as  $K^1$ .

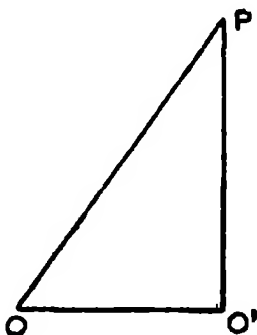


FIG. 2

Considering O, O', P as three points in the frame K, we get

$$c^2 t^2 = u^2 t'^2 + c^2 t'^2$$

$$t' = t \left( 1 - \frac{u^2}{c^2} \right)^{-\frac{1}{2}}$$

Also the distance OO' is  $l$  or  $ut'$  when measured by K, while the same distance is  $l'$  or  $ut'$  when measured by K<sup>1</sup>. Thus

$$\frac{l}{l'} = \frac{t}{t'} = \left( 1 - \frac{u^2}{c^2} \right)^{-\frac{1}{2}}$$

We have seen here that the same distance OO' is measured as  $l$  by one observer and as  $l'$  by another. Similarly the same duration of time is measured by one as  $t$  and by the other as  $t'$ . There is no reason why the measure  $l$  or  $l'$  should be preferred to the other and hence the concept of absolute length becomes futile when it comes to the measurement of it. In the same manner the clocks of K and K<sup>1</sup> may be synchronized at any chosen moment but as the same duration is given by different measures on the two clocks the events that are simultaneous to K are not so for K<sup>1</sup> after  $t=0$ , hence the concept also of the absolute simultaneity fails.

The effect on the moving rod is sometimes called the Fitzgerald or the Lorentz contraction and the slowing up of time in the moving frame, the Einstein dilatation. These effects may be deduced straight-away from the Lorentz transformation itself. Take two points  $x_1$  and  $x_2$  in the frame K corresponding to points  $x'_1, x'_2$  in K<sup>1</sup> at a certain instant  $t$ . Then

$$x'_1 - x'_2 = B(x_1 - x_2)$$

As  $B > 1$  the observer in K will say that the observer in K<sup>1</sup> will find on measurement the distance,  $x_1 - x_2$ ,  $B$  times greater. From this K will deduce that the rod in K<sup>1</sup> is  $B^{-1}$  times as short as the measuring rod in K. This contraction of the rod K attributes to the motion of K<sup>1</sup>. Similarly, choose two time-epochs  $t_1$  and  $t_2$  at any point  $x$ . Then from the transformation, if  $t'_1$  and  $t'_2$  are the corresponding instants,

$$t'_1 - t'_2 = B(t_1 - t_2)$$

K finds that according to the clock of K<sup>1</sup> the duration  $t_1 - t_2$  is  $B$  times greater. In other words K<sup>1</sup> thinks that in the moving frame K the clock runs slow.

Although neither the space-interval nor the duration of time is invariant for Galilean transformations there is a new entity  $S$  which remains invariant. This is defined by

$$S^2 = c^2(t_2 - t_1)^2 - (x_2 - x_1)^2 - (y_2 - y_1)^2 - (z_2 - z_1)^2 \text{ and hence}$$

$$\text{also } S^2 = c^2(t'_2 - t'_1)^2 - (x'_2 - x'_1)^2 - (y'_2 - y'_1)^2 - (z'_2 - z'_1)^2$$

It is clear from this that space and time, considered individually reduce to secondary importance in relativity.  $S$  is called the "interval"

between two events viz.,  $x_1, y_1, z_1, t_1$  and  $x_2, y_2, z_2, t_2$ . The interval may be broken by different observers into different sections of space and time. This does not however mean that space and time are really on the same footing in the theory of Relativity. Only one is complimentary to the other. For if we look at the very form of  $S^2$  the coefficient of  $(t_2 - t_1)^2$  is positive while that of  $(x_2 - x_1)^2$  is negative. Moreover in the very deduction of the Lorentz transformation Einstein makes use of two independent principles, one, that of the relativity of the rod and the other, that of the relativity of the clock. The rod and the clock are the two ultimate unanalysable concepts of the theory of relativity. It is, therefore, utterly wrong to say that relativity has removed the distinction between space and time.

All this new philosophy arose, as we have seen, because the absolute motion of the earth in ether has defied all experiments made to determine it. Now not only the absolute motion of translation cannot be determined but the absolute motion of rotation also is beyond the means of experiment. It has often been suggested that this latter motion should become manifest through the centrifugal forces that evolve with it. Newton, himself, was of the opinion that the absolute motion of rotation of the earth can be determined from a knowledge of the centrifugal forces. Mach objects to it on grounds that the centrifugal forces can arise also in a relative motion of rotation, that if the earth is supposed to be at rest and the framework of stars be supposed to be rotating there would be no data from our sense perceptions to distinguish this view from the current one and that the centrifugal forces might therefore arise, very naturally, also in this case. The story of an interesting experiment hangs here. Newton<sup>6</sup> proposed the rotating bucket experiment to demonstrate the existence of absolute rotation. A bucket about half full of water, was kept hanging vertically by a twisted wire. As the twist was released the bucket began to rotate. The water was first horizontal, but gradually the bucket imparted a motion to it till at last the bucket was stationary, and the water rotating, so as to rise from the middle to the sides of the vessel. Initially when the bucket was rotating and the water stationary there was no rise of water and Newton advances this in support of his argument that centrifugal forces do not arise in a relative motion of rotation. There is a very subtle and serious flaw in Newton's argument which Mach points out. The relative motion is not really the same in the two cases considered by Newton. In one case the water rotates not only relative to the sides of the vessel but to the fixed stars as well, while in the other only the vessel and not the stars are rotating relative to the still water.

This brings us directly to the idea of fields of force to be

associated with matter in motion generally. In the natural philosophy of Newton, space and time were something like definite markings on a large handkerchief. Suppose for a moment that all the objects of the universe lie on one such handkerchief of a four-dimensional extent. The masses and motions of these objects are studied under the influence of forces with the help of the space-time markings. On the other hand, in the new philosophy the four ends of the handkerchief are tied together by the law of the velocity of light. The objects inside disappear from our view and creases on the cloth come into view. The creases alter as the bodies move inside. Each body has its own field of force which is revealed by the creases on the handkerchief. The general theory of relativity is concerned with the study of the curvatures in space and time introduced by matter and motion.

The concept of a curved space-time is strictly foreign to the reader of relativity. Its implications are deeply rooted into the subject and we shall discuss them briefly later on. We will content ourselves for the present merely with indicating how relativity has changed the philosophy of mass. In relativity fields of gravitation can be intense enough to defy exploration. It is not, for example, possible to explore a centrally condensed mass. Suppose we have a large pole going out of such a mass and a monkey runs down it with a rod and a clock then he will never reach the centre of the mass. As to why this should be so we will learn from the general theory of relativity.

In the general theory of relativity we do not confine ourselves to the Galilean frames only. The Lorentz transformation ceases, therefore to fill the theatre of action from now on, new objects called tensors come into view.

To understand the tensors consider first the restricted principle of relativity, which says that all laws of Nature are covariant with respect to the Galilean frames. In the general theory we want equations to indicate the covariance of the laws with respect to all possible co-ordinate systems. A tensor, equated to zero, furnishes an equation of this type which accounts for the importance of the tensors in the general theory. It is very important to know which relations are good for all the co-ordinate systems and which are valid only for a certain co-ordinate system. Suppose we look at a man sitting on a table through a number of convex lenses, using one at each time. One of the impressions that will ever persist while these observations are being carried out is that a man is sitting on the table. But we would have different impressions about the sizes and inclinations of the legs of the table or of the face of the man. That the legs of the table are uniform may be an impression when

there is no convex lens but that certainly does not always remain the impression, and hence this is not anything like a tensor relation while the other observation, viz., that the man and the table are together is of the tensorial character.

A tensor equation looks something like the following.—

$$A \begin{matrix} i_1 & i_2 & \dots & i_p \\ j_1 & j_2 & \dots & j_q \end{matrix} = 0$$

The symbol on the left hand side is called a tensor of the order  $r$  where  $r = p + q$ , it is further said to be contravariant in  $p$  suffixes and covariant in  $q$  suffixes. The above equation really stands for  $n^r$  equations where the  $r$  suffixes  $i_1, i_2, \dots, j_q$  can each take up any of the values 1, 2, 3, . . . . . to  $n$ . Analytically two tensors are alike when they have the same suffixes at the top and the same suffixes at the bottom, in both the places the order of the suffixes also being preserved. When there is no suffix attached to a symbol the latter is called a scalar. A single suffix gives a vector, contravariant or covariant according as the suffix is at the top or at the bottom. Essentially there is no distinction between a covariant and a contravariant vector. If a matrix  $A$  transforms a covariant vector into another the matrix  $(A^1)^{-1}$  transforms a contravariant vector into another. But if we call  $B = (A^1)^{-1}$ ,  $(B^1)^{-1} = A$ . The dash is used here to indicate that the rows and columns are interchanged. Analytically there are two types of vectors, those which are transformed by the matrix  $A$  and those which are transformed by the matrix  $B$ . Either type may be called covariant the other type being then considered to be contravariant.

In the general theory, an infinitesimal interval  $ds$  is defined by

$$ds^2 = \sum^i \sum^\mu g_{\mu}^{\mu} dx^\mu dx^\mu$$

$$\Gamma = 1 \mu = 1$$

$g_{\mu}^{\mu}$  is the fundamental tensor of Relativity. Davidson and Germar<sup>1</sup> considered a number of tensors generated by  $g_{\mu}^{\mu}$ . The gravitational equations of Relativity are

$$G_{\mu}^{\mu} - \lambda g_{\mu}^{\mu} = -K (T_{\mu}^{\mu} - \frac{1}{2} T g_{\mu}^{\mu}).$$

Where  $G_{\mu}^{\mu}$  is the contracted Riemann-Christoffel tensor,  $T_{\mu}^{\mu}$  the energy tensor,  $K$  stands for  $\frac{8\pi G}{c^2}$ , where  $G$  is the gravitational constant.

The term  $\lambda$  is the cosmological term. It was Einstein who proposed first this small correction to his relativity equations to get a finite spherical universe. Later, in his exposition, Eddington has attached some philosophical significance to this step, which, however, has not been widely accepted. It was only last year that Einstein

proposed to do away altogether with  $\lambda$ . Eddington and a large number of other relativists are not prepared to take this step. We shall come to this topic again later on.<sup>8</sup>

The units that are commonly used in relativity are called natural units and might prove to be of some interest here. In the natural units the gravitational constant  $G$  and the velocity of light  $c$  are both unity, and the unit of time is the second. The unit of length therefore is  $3 \cdot 10^{10}$  cms., and the unit of mass is given by  $G = M^{-1} L^3 T^{-2}$  i. e.,  $6.65 \times 10^{-8} = M^{-1} (3 \cdot 10^{10})^3 \cdot (1)^{-2}$  or  $M = 4.06 \times 10^{38}$  gms, which is the unit of mass. This is rather a large unit for the mass of the sun turns out to be only  $\frac{2.70^{33}}{4.06} \times 10^{38}$  i. e.,  $\frac{1}{2} \cdot 10^{-3}$  units approximately. Now comes a very interesting point. Mass in relativity is recognized, usually, either from its inertial aspect in which case  $m = \frac{1}{2} \cdot 10^{-3}$  units or as a region of singularity of a certain radius. In the latter case, of course, it is convenient to express mass in units of length. Now a unit of length here is  $3 \cdot 10^{10}$  cms., and, therefore, the mass of the sun might be expressed as 1.5 kms

Let us now consider the question of the interaction between mass and space. The Schwarzschild solution for a particle of mass  $m$  is of the form

$$ds^2 = - \left(1 - \frac{2m}{r}\right)^{-1} dr^2 - r^2 (d\theta^2 + \sin^2 \theta d\phi^2) + \left(1 - \frac{2m}{r}\right) dt^2$$

It is obvious that the 'radius' of the sun as defined above is 3 kms. It becomes clear even from the study of the internal field of a body of spherical symmetry that

$$2m < a$$

where  $a$  is the radius of the sphere. Let  $\rho$  be the average density of the mass. Then  $\rho < \frac{3}{8\pi} a^{-3}$ .

Given the average density of a sphere there is thus a limit on the radius of the sphere. Thus when the average density is that of water it can be shown that the radius of the sphere cannot exceed about 400 million kilometres. We should remark here that the limit on the radius given here is applicable to all spheres with a radial distribution, the case considered by Schwarzschild being only a particular case viz., that of a homogeneous sphere.

Why should there be a limit at all in relativity on the radius of a material sphere? The reason is this: matter by its very presence makes the space about it curved so that as matter begins to be packed about a point the space about it gradually curves so that ultimately no more matter can be introduced inside.

Emden's equation for a polytropic gas sphere of degree  $n$  is of the form

$$x^2 \theta^n + \frac{d}{dx} \left( x^2 \frac{d\theta}{dx} \right) = 0$$

Where  $x$  is the "reduced" radius and  $\theta$  the "reduced" temperature. We have worked out purely out of mathematical interest the relativistic analogue of this equation which is

$$x^2 \theta^n + \frac{d}{dx} \left[ \frac{x^2 \frac{d\theta}{dx} + A x^2 (\theta^{n+2} + \theta^{n+1} +)}{1 + A\theta - 2(n+1) A x \frac{d\theta}{dx}} \right] = 0$$

Here  $A = \frac{p}{\rho\theta}$ ,  $p$  being the pressure and  $\rho$  the density, both expressed in natural units  $x$  is such that at the surface of the sphere  $x=1$ . In Milne's theory of the stellar structure the question of a centrally condensed sphere comes to the front. In a model of this type the condensation at the centre may be great enough to make the application of the relativistic correction necessary. It is with this end in view that we first attempted to obtain the above analogue.

Another question that we have found of some interest to discuss is whether space can hold condensed radiation under its own gravitation. The mathematical formulation that we have made of this question is as follows: is it possible to have a distribution of matter for  $r \leq a$  such that  $\rho = \rho(r) = 3p$  where  $\rho$  is the density and  $p$  the pressure? The result of our investigation is that radiation cannot condense in this manner.

There are several properties of the distribution of matter which satisfies a line-element of the form

$$ds^2 = + g_{11} dx_1^2 + g_{22} dx_2^2 + g_{33} dx_3^2 + g_{44} dx_4^2$$

where  $g_{11}$ ,  $g_{22}$ ,  $g_{33}$ , and  $g_{44}$  may be all functions of  $x_1$ ,  $x_2$ ,  $x_3$  and  $x_4$ . We shall go into all of them, but mention here one which we have found to be of special interest. It is that at each point of the three dimensional space  $p (dv)^{\frac{4}{3}}$  is a function only of  $x_1$ ,  $x_2$ , and  $x_3$  where  $p$  is the pressure and  $dv$  the elemental volume at the point in question. We may call this the adiabatic law for the expansion of space as in deriving it we have used the property that the proper mass of the element  $dv$  remains unchanged in time.

We come now from the interior of a material body to its exterior.

Let us consider now the external field of a point mass.<sup>9</sup> The empirical value of  $\pi$ , determined in the sun's gravitational field, is certainly different from the value of  $\pi$  known in pure mathematics. The radial distance from  $r=r_0$  to  $r=r_1$

$$\text{is } d = \int_{r_0}^{r_1} \frac{dr}{1 - \frac{2m}{r}} = \left[ \sqrt{r(r-2m)} + 2m \log (\sqrt{r-2m} + \sqrt{r}) \right]_{r_0}^{r_1}$$

We shall take  $r_0 > 2m$ . If  $\frac{m}{r_0}$  is very small

$$d = r_1 - r_0 + m \log \frac{r_1}{r_0} \text{ approximately}$$

The empirical value of  $\pi$ , say  $\pi^1$ , will be given by  $\pi^1 = \pi \frac{r_1 - r_0}{d}$

$$\text{Hence } \frac{\pi - \pi^1}{\pi} = \frac{m}{r_1} \log \frac{r_1}{m}, \text{ if } r_0 = 0 (m)$$

If we take for  $m$  the mass of the sun and for  $r_1$  the average distance of the earth from the sun we find that  $\pi^1$  differs from  $\pi$  in the sixth decimal place.

We will wind up with considerations respecting the bending of light which at once attracted the public attention and proved a genuine test of the theory of relativity. We know that a particle having a finite velocity at infinity describes a hyperbola under the gravitational attraction of another mass. If we take a corpuscle of light moving with velocity  $c$  its path under the action of the sun would be a hyperbola, the velocity is, of course, supposed to be  $c$  not everywhere but only at the perihelion. The angle between the two asymptotes gives the deflection of the path of light and is found to be  $\frac{2m}{R}$ , when small where  $m$  is the mass of the sun and  $R$  the distance from

the sun at the perihelion. From relativistic considerations we get for our deflection  $\frac{4m}{R}$  in the same problem. In relativity the deflection is

obtained by considering the field of the sun. The geodesics of the field are assumed to be the possible paths of lights as well as of small particles. The particle problem is this We consider a star occulted by the sun. If the light really bends round the sun as theory predicts it should be possible to photograph the star even when it is occulted. But such a photograph could be taken only at a total eclipse of the sun for under other circumstances the stellar image would be lost sight of on the photographic plate. In order, therefore, to calculate the bend of light it is necessary to predict from where and when a total eclipse of the sun would be visible. To add to this a known star must then be occulted by the sun. Only when all this is done and the weather conditions and the local conditions are favourable the necessary experiment can be started.

Freundlich<sup>(20)</sup> has suggested that the relativistic effect on light is not large enough to account for the observed result. It has been suggested in this connection that the gravitational equations of relativity have not yet attained to their final form and that, perhaps, they could be so re-written as to remove this difficulty. I understand that the



solar eclipse for which expeditions were sent to America last July was not favourable for making any new test on the band of light.

A certain interesting aspect of the mathematician's mind has been brought to light in a recent book, "*The World of Science*" by a mathematician of repute, Prof H Levy. It was said by one of those cynics whom one meets on the London embankment that Sir James Jeans is the Pope and "*The Mysterious Universe*" the Bible of modern science. The same cynic might have called Prof H Levy a Martin Luther. For the latter challenges the significance of one of the most easily accepted criteria of scientific advance. This criterion is what is called the simplicity criterion according to which the simplest law is chosen when alternative laws can be found to fit facts. Prof. Levy argues that the criterion is meaningless as "simplicity" itself is not mathematically defined. What is simple from one point of view may not at all be so from another. Suppose we want to find out the simplest mathematical law connecting  $x$  and  $y$  which would be in conformity with the following five pairs of values

$$\begin{array}{l} x=1 \quad x=4 \quad x=9 \quad x=16 \quad x=25 \\ y=2 \quad y=4 \quad y=6 \quad y=8 \quad y=10 \end{array}$$

One might consider (vide H Jeffreys "*The Scientific Inference*") the simplest law in agreement with facts to be  $y^2 = 4x$ . But an alternative law according to which  $y=0$  for all values of  $x$  except the five may be called with equal justification the simplest law.

I do not think the question of simplicity deserves to be treated in cold blood like this. It really arises on the frontier of science where the leading scientists are continually engaged in a guerilla warfare. All the mathematical laws which fit in with known facts are in the field so long as they help further inferences and predictions. Only that law which is most fruitful in predictions ultimately survives the rest. The surviving law is more easily assimilated than the alternative, less successful laws and is naturally treated as the simplest. Thus the simplicity of the law may be due not to anything intrinsic but to our getting more familiar with it.

A position arises in relativity where the need of the simplicity criterion is felt. There are three invariants  $K = G$ ,  $K^1 = G_{\mu\nu}$ , and  $K'' = B_{\mu\nu\sigma}^{\rho} B_{\mu\nu\sigma}^{\rho}$  whose covariant derivatives with respect to  $\delta_{\mu\nu}$  furnish when equated to zero three alternative laws which are consistent with the laws of the conservation of energy and momentum. The law corresponding to  $K$  has been now in the field. The reason for choosing this particular law in preference to the other laws is that it has been most successful in its applications. One is also led to believe that this most successful law is the simplest of the three to work with.

Of the new principles that the theory of relativity has brought in its train those of equivalence and identification deserve a place here. The principle of identification has to be very frequently used in special problems of relativity. The idea behind it may be very easily explained. A vital equation of a problem which should be tensor equation cannot often be put down for want of knowledge of the necessary tensor. But it is possible sometimes to formulate the equation in a certain set of co-ordinates. Suppose then that we hit upon a tensor whose components in the chosen co-ordinate system are the same that we have used then we look upon this tensor as the required tensor by the principle of identification. This principle has been used in equating the components of an energy tensor with multiples of those of the contracted Riemann-Christoffel tensor. The general gravitational equations of relativity were first written down in the cartesian co-ordinates and were taken over to the tensorial form by the use of the principle of identification.

The principle of equivalence is, comparatively, of greater importance, in the formal development of the theory. According to this principle some of the differential equations which are true for a flat space-time are also taken to be true for a curved one. There is no *a priori* reason for doing so in a particular case. The method followed here is simply to try and see. When the method is successful appeal is made to the principle in question, when it fails it is not the principle that is blamed but the equation under consideration!

Talking generally, in applying both the principles mentioned above the procedure adopted is the same. Starting from certain assumptions we deduce first their logical consequences to some length. Then we try to proceed backwards by inference from certain data which are either empirical or which still hold the field because of their success. The processes of deduction and induction are thus welded together at some point where an appeal is made to one of the two above principles.

We shall now try to present one or two problems in the theory of relativity that have occurred to us. We propose to consider two kinds of static solutions of Einstein's field equations for gravitational phenomena. firstly, those which give the field inside and in the neighbourhood of a condensation, and secondly, those which give static universes. Our own universe is now considered to be expanding but as the cause of the expansion from an initial state, static and unstable, is not yet fully explored it may be worthwhile to discuss different static states that are mathematically and physically possible. However some considerations will be first presented about the solutions of the field-equations in general.

The form of the line-element that comes very frequently in cosmological discussions is

$$ds^2 = -\theta_1^2 dx_1^2 - \theta_2^2 dx_2^2 - \theta_3^2 dx_3^2 + \theta_4^2 dx_4^2$$

where each  $\theta$  is a function of  $x_1, x_2, x_3$ , and  $x_4$ . If we put  $\theta_1 dx_1 = dX_1$ ,  $\theta_2 dx_2 = dX_2$ , etc.,  $X_1, X_2, X_3$ , and  $X_4$  become, in general, quasi-coordinates. If only the principal components of the energy-tensor exist the relativity equations reduce to the following,

$$-\frac{\Delta_1^2 \theta_1}{\theta_1} - \frac{1}{\theta_2} \frac{d^2 \theta_2}{dX_1^2} - \frac{1}{\theta_3} \frac{d^2 \theta_3}{dX_1^2} - \frac{1}{\theta_4} \frac{d^2 \theta_4}{dX_1^2} = \lambda - 8\pi (T_1 - \frac{1}{2}T)$$

$$-\frac{\Delta_2^2 \theta_2}{\theta_2} - \frac{1}{\theta_1} \frac{d^2 \theta_1}{dX_2^2} - \frac{1}{\theta_3} \frac{d^2 \theta_3}{dX_2^2} - \frac{1}{\theta_4} \frac{d^2 \theta_4}{dX_2^2} = \lambda - 8\pi (T_2 - \frac{1}{2}T)$$

$$-\frac{\Delta_3^2 \theta_3}{\theta_3} - \frac{1}{\theta_1} \frac{d^2 \theta_1}{dX_3^2} - \frac{1}{\theta_2} \frac{d^2 \theta_2}{dX_3^2} - \frac{1}{\theta_4} \frac{d^2 \theta_4}{dX_3^2} = \lambda - 8\pi (T_3 - \frac{1}{2}T)$$

$$-\frac{\Delta_4^2 \theta_4}{\theta_4} + \frac{1}{\theta_1} \frac{d^2 \theta_1}{dX_4^2} + \frac{1}{\theta_2} \frac{d^2 \theta_2}{dX_4^2} + \frac{1}{\theta_3} \frac{d^2 \theta_3}{dX_4^2} = \lambda - 8\pi (T_4 - \frac{1}{2}T)$$

Besides these there are the six equations

$$\frac{\Delta_1 \theta_2}{\theta_2} - \frac{\Delta_2 \theta_1}{\theta_1} = 0, \frac{\Delta_3 \theta_1}{\theta_1} - \frac{\Delta_1 \theta_3}{\theta_3} = 0, \text{ etc., etc.,}$$

In the above  $\Delta_1^2$  stands for the Laplacian operator for

$$\theta_1^2 dx_1^2 + \theta_2^2 dx_2^2 - \theta_4^2 dx_4^2, \text{ similarly for } \Delta_2^2, \Delta_3^2 \text{ and } \Delta_4^2$$

As regards the six operators of the type  $\Delta_{14}$  we have

$$\Delta_{14} \equiv \frac{d^2}{dx_1 dx_4} - \frac{d \log \theta_1}{dx_4} \frac{d}{dx_1} - \frac{d \log \theta_4}{dx_1} \frac{d}{dx_4}$$

This type of operation is also associated with the name of Laplace and the operator is known as the Laplacian operator of the second kind.

A most general discussion of the above ten equations would be beyond our scope. But we can suggest a way for obtaining new particular solutions. For this split up the last six equations into the following twelve

$$\Delta_{12} \theta_3 = \Delta_{13} \theta_4 = 0, \Delta_{23} \theta_1 = \Delta_{24} \theta_2 = 0, \text{ etc.}$$

We have obtained some particular solutions by solving these sixteen equations which we hope to publish in detail elsewhere. Here we shall merely content ourselves with the remark that some of the most well-known solutions belong to our group, *vis.*, Lemaitre's solutions and Schwarzschild's for a particle

We do not think that the general field of a nebula has been worked out, even to the first approximation in any of the standard text-books or memoirs on relativity. The result of our examination yields the following line-element

$$ds^2 = -\left(1 - \frac{4\pi}{3}\rho r - \frac{1}{6}\lambda r - \Phi\right)(dx^2 + dy^2 + dz^2) \\ + \left(1 + \frac{4\pi}{3}\rho r + \frac{1}{3}\lambda r + 4\pi\rho r^2 + \Phi\right)dt^2$$

Here  $\Phi$  stands for  $\frac{2m_1}{r_1} + \frac{2m_2}{r_2} \dots \dots \dots \frac{2m_n}{r_n}$  where

$m_1, m_2, m_3, \dots \dots \dots m_n$  are supposed to be  $n$  masses whose distances from the current point are  $r_1, r_2, \dots \dots \dots r_n$  respectively. Also the solution gives that  $\rho$  may be a function of time in which case  $\rho - 3p$  remains constant.

The working out of this problem up to the second order is beset with almost insurmountable mathematical difficulties. The relativistic analogue of the problem of two bodies has not yet been solved. It is perhaps worthwhile looking into the problem of two fixed point-masses. We find that the line element to be taken for the exploration of the field is in dipolar co-ordinates of the form

$$ds^2 = -A \operatorname{Cosec}^2 \Phi (dr_1^2 + dr_2^2) + 2B \cot \Phi dr_1 dr_2 \\ - \frac{1}{4a^2} r_1^2 r_2^2 \sin^2 \Phi d\Phi^2 + c^2 dt^2$$

where  $r_1, r_2, \sin \Phi$  is twice the area of the triangle formed by current point and the fixed positions of the two masses,  $A, B, C$  are all functions of  $r_1$  and  $r_2$  to be determined by solving the relativity equations. The differential equations that arise in this investigation have not yet been completely solved.

## RELATIVITY AND COSMOLOGY

### II

Cosmology deals with the origin of the universe and cognate problems. Once it was all talk—mere speculations—but now, and particularly since the advent of the theory of relativity cosmology is being guided by mathematical thought. Even in relativistic cosmology the speculative element is quite conspicuous and from the nature of the subject it is difficult to believe that this element could ever be wiped out of the subject.

It was Einstein who started the study of the world from the relativistic point of view. The theory of relativity had already been found more successful than gravitation for the phenomena of the Solar system. It was therefore natural to extend this theory as Einstein did to a much larger system, *vis*, the world as a whole. Such an extrapolation, it should be remembered, was also made by Newton and it met at the time with an amazing success.

Einstein presented in his earlier discussions two reasons for believing the world to be finite. His first reason was not acceptable to

many and it was supposed to be due to the influence that Mach exercised over him. Mach contended that the inertia of a body increases when the other bodies in the universe are brought nearer to it. Einstein showed that this could be true only in a finite universe.

The other argument was more convincing to mathematicians. If the celestial bodies were subject only to the gravitational influence then the mean velocities of the stars of a cluster would be, as it has been found out, much greater than what they actually are. This shows that there is an all-pervading field of force which diminishes the influence of gravitation. Now it is the property of a finite static world to have such a field. These considerations led Einstein to take for a model of the universe a finite and unbounded one as presented by one of his solutions of the relativity equations

Let us now consider some of the questions that have been provoked by the phrase "a finite and unbounded universe". The universe can be at once finite and unbounded just as a circle can be said to be so because its length is finite while it has no beginning or end i.e., no boundaries. Similarly a sphere has a finite surface and is still unbounded. The Einstein universe is a hypersphere whose surface is three-dimensional. Mathematically the departure from the familiar sphere to the hypersphere is a mere matter of taking one more variable while mentally the hypersphere defies conception. It is only by those who cannot conceive of a hypersphere the question is asked as to what is outside the universe, if it is finite. This enquiry is generally due to the associated idea that a sphere can be perceived outside another. Well! This is so because the two spheres exist in a three-dimensional space that can be explored by our senses. Similarly a hypersphere may exist outside another but the two form part of a four-dimensional space which cannot be explored by the senses. Thus we can pass from our finite universe to another "outside" only if we can stretch our limbs in the fourth dimension. This fourth dimension is space and should not be confused with what usually stands for the time-dimension.

The Einstein universe is characterized by a homogeneous distribution of matter, absence of pressure, and a linear relation between the total mass and the radius of the universe, viz.,

$$\frac{MG}{c^2} = \frac{\pi}{4} R$$

Here  $M$  is the total mass, relative or proper, it is the same as there is no pressure.  $G$  is the gravitation constant,  $c$  the velocity of light and  $R$  the radius of the universe. The linearity of the relation between  $M$  and  $R$  first came as a surprise to many but it can be derived even from purely gravitational considerations. Let  $R$  be the radius of a sphere and  $M$  the total mass contained in it. If this sphere is a very close model of the universe there must be something at the

surface of the sphere to limit the extent of the universe. The boundary condition we can think of is that radiation follows along the surface of the sphere. If we take the centre of the sphere as the centre of gravity of all the masses and  $c$  for the velocity of radiation, we have by equating the accelerations at the boundary,

$$\frac{MG}{R} = \frac{c}{R} \quad \text{or } M.G = c^2 R$$

Another interesting interpretation of this relation is that it defines the gravitational constant in terms of the total mass and the size of the universe

There were two serious objections to Einstein's theory. One was that Einstein's universe is devoid of motion and another that a condensation of matter cannot exist in the universe. The actual universe is full of both motion and condensations and hence the Einstein's could not be considered a successful model of the universe.

An alternative solution of Einstein's relativity equations gave De Sitter another model for the universe. This is called the De Sitter universe. It is isotropic in space and time but devoid of matter. A powerful field of repulsion occupies the whole universe so that any particle introduced into it is repelled from the centre. Evidently as a model the De Sitter universe is as unsatisfactory as the other. But it is clear that the properties of the models are complementary and the required model for the universe lies somewhere between these two extremes.

Before considering a series of solutions of Einstein's equations from Einstein's to De Sitter's let us note a property of the latter. The time-element for De Sitter's universe may be expressed in the form

$$ds^2 = -R^2 [dx^2 + \sin^2 x (d\theta^2 + \sin^2 \theta d\phi^2)] + \cos^2 x dt^2$$

At  $x = \frac{\pi}{2}$  the time comes to a standstill, and this plane, therefore gives what is called the horizon of the universe. The horizon was first interpreted by Weyl as the seat of matter in this universe but this view has found no support. All singularities and eccentricities associated with a space-time frame cannot be necessarily due to the presence of matter; some of these may be purely of a mathematical interest and they can be transformed away.

All the static spherical universes that have both matter and motion have a line-element of the following form

$$ds^2 = -R^2 [dx^2 + \sin^2 x (d\theta^2 + \sin^2 \theta d\phi^2)] + (A - B \cos x)^2 dt^2$$

where  $A$  and  $B$  are arbitrary constants.  $B=0$ ,  $A=\pm 1$  give the Einstein universe while  $A=0$ ,  $B=\pm 1$  gives the De Sitter universe.

The pressure  $p$  and the density  $\rho$  are distributed according to the following formulae :

$$8 \pi p = \lambda - \frac{1}{R^2} + \frac{2 B \cos x}{R^2(A - B \cos x)}$$

$$8 \pi \rho = -\lambda + \frac{3}{R^2}$$

$$\frac{\partial p}{\partial x} + (p + \rho) \frac{B \sin x}{A - B \cos x} = 0$$

For those models for which  $\left| \frac{A}{B} \right| > 1$  there is no horizon while for

those for which  $\left| \frac{A}{B} \right| \leq 1$  there is. The models of the latter group

are obviously of no physical interest and of the former group only a few which have the pressure and density everywhere non-negative are of some interest. Even here the uniform distribution of matter on the one hand and the uneven distribution of pressure on the other make these few models extremely artificial; and although they are so we have mentioned them as they have not received any notice in the general literature on cosmology.

The solution which was first discovered (1923) by Friedmann and later independently rediscovered (1930) by H. P. Robertson and Lemaitre gives the well-known theory of the expanding universe. It should be remembered that De Sitter's solution had one special advantage over Einstein's, *viz.*, that it admitted the recession of such distant objects as the spiral nebulae. A study of the geodesics in de Sitter's universe shows that bodies at a distance from the centre move with velocities proportional to their distances. Now the spiral nebulae are the most distant objects known to the astronomer. They are being studied spectroscopically for fifteen years. The reddening of the light coming from these nebulae has been attributed primarily to their recession. But the recession could not give any support to De Sitter's theory until it was observed that all the spiral nebulae are receding. On a careful examination some of the spiral nebulae turned out to be exceptions. Later on these exceptions were explained away by the motion of the Solar system as whole. Hubble and Humason who have been engaged on the problem of the spiral nebulae for the last ten years present a linear relation between the distances and velocities of the spiral nebulae. The observational data in support of the linearity are not yet as satisfactory as they should be. The theory of the expanding universe has come into prominence mostly because it is in agreement with the linear relation.

We cannot pass on to the theory of the expanding universe without referring to two vital objections to it. One is that the reddening of the light may be due to the photons losing their energy

in collision on their way to us from the distant nebulae. It seems that the reddening from this source is not strong enough to account for the observed shift. Another objection is due to a similar argument advanced by Macdonald that energy might be leaking from the photon at a very slow rate on its way from the nebulae. The leakage is conspicuous because of the long time taken by light in reaching the earth from the distant spiral nebulae. So far as we know this objection has not received any consideration from the physicists.

The line-element for a non-static universe may be stated as

$$ds^2 = -R^2 [dx^2 + \sin^2 x (\theta^2 + \sin^2 \theta d\phi^2)] + dt^2$$

Where  $R$  is a function of time. The distribution of matter in the universe is subject to the equations, sometimes called Lemaitre's equations, viz.,

$$\lambda + K\rho = \frac{3}{R^3} + \frac{3\dot{R}^2}{R^4}$$

$$2\lambda - K(\rho + 3p) = 6\frac{\ddot{R}}{R}$$

where  $K = \frac{8\pi G}{C^3}$  in the usual notation and  $\dot{R}$  means  $\frac{dR}{dt}$  etc. We

cannot know from the above two equations whether the universe is expanding or contracting or oscillating. The equations simply tell us that the radius  $R$  of the hypersphere under consideration is a certain function of time obeying certain restrictions. Two methods have been used to take the problem of evolution. One method is to supplement the relativity equations with an additional one representing a physical criterion. Another method is to put  $\lambda = 0$ . Let us first study the second method.

The constant  $\lambda$  was first introduced by Einstein for cosmological considerations only. It is so small that the modification introduced by  $\lambda$  in the relativity equations is negligible for all other considerations. Thus the modified relativity equations were

$$G_{\mu\nu} = \lambda g_{\mu\nu} = -K(T_{\mu\nu} - \frac{1}{2}Tg_{\mu\nu})$$

Only the equations so modified can give the finite and unbounded static universe of Einstein. We have already mentioned that Einstein was led by several reasons to think that the universe is finite. Hence it is clear why the modification was effected.

Eddington has advanced philosophical considerations to justify Einstein's modifications. He argues that the principle of the relativity of length must be introduced to make the theory of relativity logically complete. When we say that a certain rod is ten metres long we do so by comparing it with some standard rod usually placed at a different place. Such a comparison assumes that the standard rod when moved from place to place remains unaltered which is certainly without any



justification. We therefore want a standard for comparison at any place and that is furnished by the local radius of curvature which is determined by  $\lambda$ .  $\lambda$  has the dimensions  $L^{-1}$ . For the Einstein universe  $\lambda = \frac{1}{R}$ . The length of any vector  $A^r$  is  $\sqrt{g_{ur} A^u A^r}$ .

This is connected with the invariant  $\sqrt{G_{ur} A^u A^r}$  by

$$G_{ur} A^u A^r = \lambda = G_{ur} A^u A^r.$$

in free space. Thus

$$\frac{\sqrt{g_{ur} A^u A^r}}{\frac{1}{\sqrt{\lambda}}} = \sqrt{G_{ur} A^u A^r}$$

or	$\frac{\text{the local length}}{\text{the local radius of curvature}} =$	$\text{the local value of a certain invariant.}$
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The importance of  $\lambda$  in this respect has not yet been recognised by several relativists. Einstein himself in 1931 put  $\lambda = 0$  firstly because the non static solution does not need  $\lambda$  and secondly because it has introduced a number of difficulties that have not yet been got over. Perhaps it was De Sitter who first suggested that  $\lambda$  is a constant too many in Lemaitre's equations.

It is now necessary to tell why an expanding universe is preferred to the other non-static universes. If we imagine ourselves to be at the centre of an expanding bubble we observe a scattering and recession of the marks on the bubble. Our own universe may not be a perfect sphere. It is highly irregular at places and yet a hyperspherical universe serves as a model to our own. The surface of the hypersphere is three dimensional and the planets, the stars, the nebulae etc., are landmarks on the spherical surface. Now the recession and scattering would be most conspicuous in the most distant objects. The proof of the expansion is therefore to be sought in the spiral nebulae. The spiral nebulae are observed to be receding according to the approximately linear relation between distance and velocity, viz., 600 kms per second per parsec. Eddington has been able to predict from the space interaction term in the wave equation of an electron that the velocity of recession is 528 kms. per sec. per parsec. In view of the uncertainty of the astronomical data employed here the agreement between theory and observation may be said to be remarkably close.

Let us consider now Lemaitre's equations for an expanding universe with  $\lambda = 0$  as has been suggested. Then

$$\begin{aligned} \dot{R}^2 &= \frac{3}{R^3} + \frac{3R^3}{R^3} \\ -k(\rho + 3p) &= 6 \frac{\dot{R}}{R} \end{aligned}$$

Since  $\rho$  must be ever non-negative and  $P$  always positive there cannot be a stationary state for which  $\dot{R} = 0$ ,  $R = 0$ . Moreover as  $R$  is always negative the universe will expand to a certain maximum and then contract till the matter of the universe allows it to.

A serious objection to the above theory is that it gives no satisfactory answer to the fundamental question as to how the expansion arose or what the initial state of the universe was. It has therefore been found necessary by certain investigators to keep  $\lambda$  as it is and to supplement the relativity equations with a criterion to obtain a solution.

It is fair to state in the very beginning that no satisfactory criterion has been discovered so far. In his original paper Lemaitre suggested that the conservation of the proper mass should be assumed with the cosmic pressure always negligible. In the real universe the proper mass is certainly not conserved as the celestial bodies (most of which are radiating) lose it in radiation, for radiation has no proper mass. That the relative mass is conserved is also an unsatisfactory hypothesis as it changes with motion. Lemaitre did sketch out in his first paper the evolution from the Einstein state which is a stationary state of Lemaitre universe. But his assumption that the pressure is negligible withstood all attempts to explain the origin of expansion in the Einstein universe.

Eddington has shown that the Einstein universe is unstable. According to him it is quite a reasonable hypothesis that the Einstein state was one of the initial states of the universe. In this model there is a homogeneous distribution of matter. In the universe as it is most of the matter has been condensed into stars and nebulae. The question that now strikes one is whether the expansion arose owing to the formation of condensations in the Einstein universe. There is one difficulty at the outset, that of the time-scale. It is estimated that the stars are about  $10^{18}$  years old while the expansion is, comparatively quite a recent phenomenon as it could have arisen only  $10^{10}$  years ago. De Sitter is serious about this difficulty while Eddington takes the view that once the problem of the expansion is solved reasons may be found out to bring the age-limit of the stars much nearer to  $10^{10}$  years.

Confronted with the above question McVittie and McCrea started with building a mass condensation in the Einstein universe so as to see whether the volume of the universe thereby increases, the total proper mass being supposed to be conserved. They started with two different line-elements and obtained contrary results. There is nothing puzzling about them as it was doubtful whether the mathematical singularities considered by them were mass-points at all. Later on they discovered another mistake in their calculations and have now come to the conclusion that the second order terms will have to be

considered to know whether the increment in volume is positive or negative.

It seems to us that the real difficulty in the procedure is due to the mass-point being not well defined. The problem of a mass placed in the Einstein world must be first solved, the equations governing the field of the mass must be fully solved, and then only we can consider the effect of the formation of condensations on the Einstein universe. In a static universe the field outside an isotropic singularity is given by the line-element

$$ds^2 = -e^{\mu} dr^2 - r^2 (d\theta^2 + \sin^2 \theta d\phi^2) + e^{\nu} dt^2$$

where  $\mu$ ,  $\nu$  and  $\rho$ ,  $\rho$  are governed by the following field-equations.

$$\frac{e^{\mu}}{e} = 1 - \frac{2M}{r} - \frac{\lambda}{3} \left( r^2 - \frac{a^2}{r} \right)$$

$$\frac{-\mu}{e} \frac{\partial r}{\partial r} = k\rho r + \frac{2M}{r^2} - \frac{\lambda r}{3} \left( 2 + \frac{a^2}{r^2} \right)$$

$$\frac{\partial \rho}{\partial r} = -\frac{1}{2} (\rho + \rho) \frac{\partial r}{\partial r}$$

$$\text{where } M = \frac{K}{2} \int_a^r \rho r^2 dr + m$$

$m$  and  $a$  being the mass and the radius of the condensation. One may at once anticipate that all singularities subject to these equations cannot be identified with mass-points whose properties are familiar, an assumption connecting the four variables  $\rho$ ,  $\rho$  and  $\mu$ ,  $\nu$  is necessary.

De Sitter who was the first to look into this question assumed  $\rho$  to be constant. His solution was only a first approximation. Silberstein, however, considers this for a higher approximation and shows that the apparent difficulties at the polar of a mass-point are real and they cannot be transformed away. Moreover, while  $\rho$  is constant  $\rho$  becomes a function of position which makes De Sitter's assumption extremely artificial. McVittie and McCrea make an assumption about  $\nu$ . This is also very unsatisfactory as one doubts as to whether the singularity obtained by them is a mass-point at all. This is certainly a vital point in the determination of the effect of condensations on the volume of the three-dimensional space since mathematical singularities of different types may lead to different results.

A criterion is therefore necessary to distinguish a mass-point from the other, mathematically possible singularities that inevitably arise in the solution of Einstein's equations. This criterion to be furnished by the external field must be of a tensorial form. For it is then that any peculiarities of the external field which are not

desirable can be transformed away if at all. A suitable criterion is furnished by the world curvature  $G$  which is given by

$$G = KT + 4\lambda$$

We see at once from Schwarzschild's solution that a mass-point in empty space does not alter  $G$ . Extending this idea to the world full of matter and motion the criterion for a mass-point to be taken is that the world-curvature is not disturbed by it. This is the extra condition necessary to supplement the field equations to determine  $\phi, \rho$  and  $\mu, \nu$ .

The above criterion also furnishes the much needed extra condition to determine the evolution of the Lemaitre universe. Consider an Einstein universe in which condensations are formed. Then everywhere except at these singular points the criterion furnishes an equation. As we have shown elsewhere this is enough to indicate that such condensations produce a tendency in the universe to expand.

We are giving in the end a number of references for those who want to pursue the subject further. It should however be remembered that no theory of cosmology can ever be complete as the observational data are ever so poor. One wonders as to what would be the theories three or four years from now when the new 200 inch telescope at Mt. Wilson becomes ready for observation!

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- (10) Freundlich; *Lecture at the Royal Astron. Society Dec. 1931*,

## THE PART OF MATHEMATICS IN THE HISTORY OF THOUGHT

*By*

D C PAVATE

The general impression of a fairly cultured man about mathematics is very vague if not blank. Probably he has a faint recollection that mathematics is concerned with elaborate formulae and bewildering constructions involving a copious use of symbols and diagrams entirely unintelligible to the majority of people. The essential features of mathematics remain unnoticed by a man of average education, still less can we expect him to understand the part it has played in the history of thought or the contribution it has made to the progress and civilization of mankind. I propose to discuss in this paper the profound influence mathematics has exercised on the thinking minds from the earliest times up till now.

It is held that Mathematical Science is the most original creation of the human spirit, though another claimant for the same honour is music. The originality of Mathematics consists in the fact that relations between things are exhibited in the Science of Mathematics which are extremely unobvious apart from the agency of human reason. On reflection we see that mathematical thought is all pervading and enters every department of mental activity. The grocer when he weighs his sugar makes use of mathematical conceptions, when he enters his receipts, he uses a notation developed by a mathematician. The engineer employs methods and concepts of mathematical thought when he is building a bridge. The philosopher reflects on space and time, on number and quantity, on matter and motion which as well belong to the regions of mathematical thought. Recent developments in the study of heredity and eugenics have been rendered possible by the powerful weapons of mathematics. The study of statistics depends on the use of graphs and mathematical calculations.

Let us stretch our imagination backwards through thousands of years and endeavour to realize the gradual development of mathematical ideas. Take the question of numbers. The number 'two' applies to appropriate groups of any entities whatsoever—to two eyes, two apples, two books, two days &c. Thus the numbers are independent of any 'aggregate' and 'aggregates' which are equivalent to one another are said to have the same number. If we compare the number 'five' to the number 'two' we are thinking of two groups of

things. It is a remarkable feat of abstraction to establish this relationship between two groups of entirely different objects. The man who discovered the analogy between a group of seven apples and one of seven days made a notable advance in the history of thought. He was the first man who established a concept belonging to the Science of Pure Mathematics.

Let us see what is the function of Pure Mathematics in thought. It is a resolute attempt to go the whole way in the direction of complete analysis so as to separate the elements of mere matter-of fact from the purely abstract conditions which they exemplify. The characteristic of mathematics is that in it we have always got rid of the particular instance and even of any particular sorts of entities. No mathematical truths apply merely to fish or merely to stones or merely to colours. So long as we are dealing with pure mathematics, we are in the realm of complete and absolute abstractions. The reason insists that if any entities whatever have any relations which satisfy such and such purely abstract conditions, then they must have other relations which satisfy other purely abstract conditions.

The second characteristic is the certainty of mathematics which depends upon its complete abstract generality. Such an abstract generality cannot be arrived at without some presupposed conditions. These are called the axioms and postulates which have not a *priori* certainty without some definitions. The third characteristic of mathematical abstraction is that our abstract postulates hold for the particular case in question. To take an example from arithmetic. It is an abstract truth that any group of forty entities can be subdivided into two groups of twenty entities. So coming to a particular case, we conclude that a particular group of 40 apples can be subdivided into two groups of apples of which each contains twenty apples. But there remains the possibility that we have miscounted the big group and one of the two heaps, on subdivision has an apple more than the other. Thus there is great room for error in the process of verification for the particular case. The function of a mathematician, therefore, is not to see whether his definitions and postulates are accurate representations of things or not in our physical universe but to see that they are not self contradictory and are mutually consistent. This is the essence of mathematical physics. When mathematical processes are applied to physics, an assumption is made that the definitions and postulates in the Science of matter are applicable to Physical phenomena. If this assumption is incorrect, the mathematical deductions disagree with experimental tests.

This love for abstract generalisation enlightens every act of the functioning of the human mind. It emphasises the direct æsthetic appreciation of human experience. Secondly there is the abstraction

of the particular entities involved, viewed, in themselves and as apart from that particular occasion of experience in which we are apprehending them. Lastly there is the further apprehension of the absolutely general conditions satisfied by the particular relations of those entities in that experience. They are conditions which might hold for an indefinite variety of other occasions involving other entities and other relations between them. These conditions are perfectly general because, they refer to no particular occasion, to no particular entities and to no particular relationship between such entities. The generality of mathematics is the most complete generality consistent with the community of occasions, which constitutes our metaphysical situation. Thus the idea of a 'variable' is introduced into mathematics and mathematical logic because, the general conditions transcend any one set of particular entities. It is by the introduction of this notion that the general conditions are investigated without any reference to the particular entities. The exercise of logical reason is always concerned with these absolutely general conditions. The harmony of the logical reason is the most general aesthetic property arising from the mere fact of concurrent existence in the unity of one occasion. Whenever there is a unity of occasion there is thereby established an aesthetic relationship between the general conditions involved in that occasion. This aesthetic relationship is that which is divided in the exercise of rationality. This reasonable harmony means that for things to be together involves that they are reasonably together.

Pythagoras who lived in the sixth century B. C. was the first man who had any grasp of the full sweep of this general principle. Though our knowledge of him is fragmentary we know some points which establish his greatness in the history of thought. He insisted on the importance of the utmost generality in reasoning. He divined the importance of number as an aid to the construction of any representation of the conditions involved in the order of nature. He studied Geometry and discovered a general proof of the remarkable theorem\* about the right angled triangles. On the side of Philosophy, he has discussion which has agitated thinkers ever since. "What is the status of mathematical entities, such as numbers, for example, in the realm of things?" The number "two" for example is in some sense exempt from the flux of time and the necessity of position in space. The same thing can be said of Geometrical notions.

Pythagoras is said to have taught that mathematical entities such as numbers and shapes, are the ultimate stuff out of which the real entities of our perceptual experience are constructed. As thus stated the idea seems to be crude and indeed silly. But undoubtedly he had

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\* The general theory as well as a general proof of it had been discovered in India long before Pythagoras discovered what is surmised to be his proof of it.

hit upon a philosophical notion of considerable importance—a notion which has moved the minds of men for centuries together. To-day when Einstein proclaims that physical facts such as gravitation are to be construed as exhibitions of local peculiarities of the properties of space and time, he is merely following the pure Pythagorean traditions. The philosophical speculations of Pythagoras reach us through the mind of Plato. The Platonic world of ideas is the refined form of the Pythagorean doctrine that the number lies at the base of the real world.

Let us examine the developments of Geometry. The subject was originated in the empirical observations of the Physical world. But it has assumed forms of ever increasing abstractions. At the time of Pythagoras it became a purely rational science and the further development of Geometry was no longer dependent on the empirical observation. In rational Geometry points, straight lines, circles etc., are dealt with not as physical objects but as abstractions from objects perceived by senses. These possess certain properties in perfection which we only approximately realise in the Physical world. For example the straight line in rational Geometry has the properties of linearity and straightness in absolute perfection, whereas these properties are only imperfectly realised in any physical object which we may take as affording an approximate idea of a straight line. The precise properties of these idealised objects are fixed by means of some scheme of definitions, axioms and postulates, the nature of which is, to a large extent but not wholly, determined by empirical observation of actual relations in the physical domain. The history of geometry is of general interest because, Geometry may be regarded as the type of rational science which every science may be expected to conform to, at the distant time when a schematic representation of the Phenomenon with which it deals, is set up.

Thus Plato and Pythagoras contributed a lot to the concepts of mathematical reasoning. Aristotle now threw emphasis on classification by his Logic. Classification is a half-way house between the immediate concreteness of the individual thing and the complete abstractness of mathematical notions. Classification is necessary but unless we can progress from classification to mathematics, our reasoning will not take us far. Thus the popularity of Aristotelian Logic retarded the advance of physical science throughout the middle ages. In the interval of nearly two thousand years between the time of Pythagoras and Plato to the 17th century, mathematics had made immense strides on technical lines but did not play much part as a formative element in the development of Philosophy. Some of the old ideas lingered on but philosophy received no fresh inspiration from the steady advance of mathematical science. In the 17th century the influence of Aristotle was at its lowest and mathematics received its



importance of the earlier period. It was an age of great philosophers and great physicists, and the physicists and philosophers were alike mathematicians. It was the age of Galileo, Descartes, Newton and Leibnitz. Mathematics was an influence of the most pronounced order in the formation of philosophic ideas. The mathematics that now came into prominence was a different science from the mathematics of the earlier epoch. It had gained in generality and begun to apply some of its results to physical science or to the philosophic thought thus helping both subjects to grow. Arabic notation of decimal system, Hindu developments of Algebra and Trigonometry had been already contributed by Asiatic thought. Thus arose the idea of a function of one or more symbols (these symbols being letters called arguments or variables). Algebra thus develops into the general science of analysis in which we consider the properties of various functions of variables. Finally the simple known functions like the algebraic functions, logarithmic functions and trigonometrical functions suggested the idea of any function, the rise of algebraic analysis led to Descartes' discovery of Analytical Geometry and then to the Infinitesimal Calculus by Newton and Leibnitz. There is no sharp distinction between algebraic analysis and the Infinitesimal Calculus except that the latter involves the process of limits.

In the 17th century this idea of a general function was dominant in the abstract sphere of mathematics and enabled mathematicians to put the laws of nature in nice and elegant forms. Mathematics thus supplied the background of imaginative thought with which the men of science approached the observation of Nature. Galileo produced formulae, Descartes and Newton did the same. It was only in the last century that the increasing complexity of both the subjects, Mathematics and Physics, produced the separation of the two departments. In the 17th and 18th century the Mathematician and Physicist were one and the same man. Mathematical thinking has played a very important part in the formation of the fundamental concepts of the Physicist. Take for example the conception of Energy and the exact meaning of the great generalisation known to us as the Principle of conservation of Energy. This principle was the direct outcome of the development of the abstract side of molar mechanics which enabled us to define K. E. & P. E. as work in measurable quantities. This mathematical expression was so elegant and so apt that it naturally got extended to the molecular domain. The doctrine of the conservation of Energy was a necessary presupposition of further development for Joule and Mayer, who regarded heat as a form of energy. Joule was able to determine the mechanical equivalent of heat only because the mechanical work was already regarded as a measurable quantity. The notion of Potential which is a fundamental

subject in Electromechanics and which is constantly employed by every electrical engineer was first developed as a mathematical conception during the 18th century in connection with the theory of attractions of gravitating bodies. It was transferred to the electrical domain by Green and others together with a good deal of detailed mathematics applicable to the potential function.

Another example of the effect of the abstract development of mathematics of the Science of those times was the notion of periodicity. We are all familiar with recurrence in our ordinary experience. Days recur, lunar phases recur, the seasons of the year recur and beats of the heart recur. The recurrence forms the fundamental basis of our knowledge. Thus in the 16th and the 17th centuries, the theory of periodicity took a fundamental place in Science. Kepler divined his three famous laws about the orbits of the planets and the periods in which the planets described their orbits. Galileo observed the periodic vibrations of pendulums. Newton explained sound as being due to the disturbance of air by the passage through it of periodic waves of condensation and rarefaction. Huyghens explained light as being due to the transverse waves of vibrations of a subtle ether. Mersenne connected the period of the vibration of a violin string with its density tension and length. The birth of modern Physics depended on the application of the abstract idea of periodicity to a variety of concrete examples.

Now the Science of Trigonometry arose long ago from the ratios between the side and hypotenuse of the right angled triangle. But under the influence of the general idea of functions it broadened out into the study of the simply abstract periodic functions. Thus trigonometry became abstract and hence useful. The theory of representation of a function of a real variable by means of trigonometric series has revolutionised the whole mathematical world. It is an indispensable weapon in the hands of a physicist and at the same time has exercised the most far-reaching influence upon the development of modern mathematical Analysis. It is indeed very surprising that as mathematics withdrew increasingly into the Heavens of great extremes of thought, it returned to the Earth with a corresponding growth of importance for the analysis of concrete fact. It seems clear now that the utmost abstractions are the true weapons with which we are to control our thought. The theory of sets of points arose directly from questions connected with trigonometric series. The precise formulation by Rieman of the conception of definite integral and the gradual development of the modern notion of a function as existent independently of any special mode of representation by an analytical expression, are further examples of the results of the study of the properties of these series upon mathematical analysis. It is significant,

however, all this had its origin in the attempt to investigate the form of a stretched string in a state of vibration. This eventually led to theory of Fourier Series.

Fourier himself did not give any complete general proof of the convergence of the Series to the value of the function. Although this problem arose from the applications to the physical phenomenon, the problem of convergence has given such an impetus to the development of the Theory of Functions. It is out of place here to narrate the whole history of the theory of Fourier Series and the brilliant researches from the point of view of abstract thought, it has led to uptil now. The subject is by no means closed even now, but I shall simply point out the ultimate progress of humanity such problems lead to. A pure mathematician is never satisfied with the Fourier Series which converges everywhere normally. Very often a mathematician's generalisation from a non-utilitarian point of view has led to astounding results. Early in the last century some of the brilliant mathematical physicists were engaged in establishing the relation between the phenomenon of Electricity and of Magnetism. They were solely actuated by intellectual curiosity in bridging the gulf between the two important phenomena. Had their spirit been utilitarian, they would have probably left the matter on one side as holding out no prospect of useful application. At last it was found that Electricity in motion produced the same effects as magnets at rest, and vice versa. The result of this discovery has enabled us to have such physical comforts as motor cars, the telephone, and the electric telegraph and various other things.

Though an all round progress was made in the 19th century in Pure mathematics, the influence of mathematics upon the general thought of the age was not considerable. Its influence was on dynamics and physics and consequently on engineering and chemistry. Yet it is difficult to overrate its indirect influence on human life through the medium of these sciences. Since the technique had been perfected its progress was easy though uninteresting.

On a retrospect we see that there are two great periods of direct influence on the history of Mankind. The first period was that stretching from Pythagoras to Plato when the possibility of the Science and its general character dawned upon the Grecian thinkers. The second period comprised the 17th and the 18th centuries of our modern epoch. In both the periods there was an awakened curiosity and a movement towards the reconstruction of traditional ways. Critical scientific interest was present in both the periods. The parallel between the two epochs must not be pressed too far. The modern world is larger and more complex than the ancient one. We are now entering upon an age of reconstruction in religion, in science and in political thought.

If we are to avoid mere ignorant oscillation between extremes, we are to seek truth in its ultimate depths. There can be no vision of this depth of truth except in a sound philosophy which takes full account of those ultimate abstractions, whose interconnections it is the business of mathematics to explore.

## THE INFINITE IN MATHEMATICS\*

By

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*"But what has been said once, can always be repeated."*

—Zeno of Elea, as quoted by Simplicius.

### 1. *Concept of Infinity Indispensable to Mathematics*

Modern analysis is nothing but the theory of infinite processes, where by an infinite process I mean a set of operations which produces an infinite sequence. On a little reflection, the statement will be obvious. The arithmetic continuum forms the central pillar that supports modern analysis, and this central pillar could not have been constructed but for the work put in by great artists like K. Weierstrass (1815-1897), R. Dedekind (1831-1916), and G. Cantor (1845-1918). In putting the theory of irrational numbers on an arithmetical basis both Cantor and Dedekind start from the domain of rational numbers. But in arriving at the domain of real numbers, the arithmetic continuum, the former explicitly uses an infinite process while the latter employs the principle of partition imposed upon an infinite set of rational numbers† Again one who is familiar with the Integral Calculus need not be told that even comparatively simple problems such as finding the length of a curvilinear arc, or the area enclosed by curved lines depend for their solutions upon an infinite process. And it is easy to go on indefinitely multiplying examples of this nature to show that the concept of infinity is indispensable to mathematics; nay, it may be even asserted, without any fear of contradiction, that but for the concept of infinity, the science of mathematics would have been poorer by the loss of modern analysis. For we knew that the *method of exhaustion*, invented by Archimedes (287 ?—212 B. C.), contained all the elements essential to an infinitesimal analysis; but the *horror infinite* which the arguments of Zeno instilled into the minds of the Greek mathematicians acted as an effective brake against all further progress in that direction for a period of no less than 1,850 years. It was reserved for J. Kepler (1571-1630) to lay down the foundations of our modern Integral Calculus by publishing his book *Nova Stereometria Doliorum* in 1615 in which he successfully used the method of

\* The subject suggested itself to me on reading *Number* by Tobias Dantzig.

† For more information on this point vide writer's *Essays in Mathematics*, No. 1, §§ 32-34.

exhaustion, coupled with the notion of infinitely small and infinitely large quantities in determining areas and volumes of curved figures; and the present structure of modern analysis has been built only during the course of the last century.

## 2. *Bounded Arithmetic and Bounded Geometry*

Again but for the concept of infinity many an operation in our arithmetic and Euclidean geometry would not be possible. For instance, if we terminate the sequence of natural numbers 1, 2, 3, . . . . at a psychological limit of the counting process, say at 1,000,000, the operations of addition and multiplication such as  $500,000 + 500,001$  and  $1,000 \times 1,001$  would be impossible in such a finite and bounded arithmetic. Similarly in geometry, should it be necessary to confine ourselves to a finite and bounded plane, it would be entirely a matter for speculation whether or no two straight lines taken at random form an angle, or three, a triangle.

## 3. *Concept of Infinity has no Experiential Basis*

Now though these primary mathematical operations of telling and measuring, leading as they do to the theory of number and of geometry, had their origin, like all other sciences, in the practical needs of man living in the physical world, all our experience of this physical world cries out the falsity of the concept of infinity. The tremendous progress that we have achieved in experimental sciences clearly indicates that there is no experimental basis for the said concept. The closing months of the last century witnessed the discovery of the Quantum Theory by M. Planck. Planck propounds that the radiant energy does not flow continuously and is not capable of being divided indefinitely, as every continuous matter should be, and that it is emitted in integral quantities or bundles, known as quanta. The recent researches carried on by Rutherford and Bohr regarding the structure of an atom lead us to the conclusion that matter is not subject to the process of infinite divisibility, it ultimately consists of electrons and protons which have finite sizes. Thus "wherever the method of investigation of matter has been carried sufficiently far, we have invariably struck a limit of divisibility, and this was not due to a lack of experimental refinement but resided in the very nature of phenomena." Again like infinite divisibility of matter—and energy is but matter in another form—"the infinitude of the universe" is now declared to be a myth. For Einstein's study of the cosmos from the view-point of his theory of gravitation leads to the possibility of a finite universe and the observations of the astronomers agree with his hypothesis of an elliptic universe.

## 4. *Nor is it a Logical Necessity*

Thus the concept of infinity is not an experiential necessity, nor is it a logical necessity. For by recasting and reconstructing

a few postulates and definitions of the present system of arithmetic it is possible to build up a conceptual scheme of finite arithmetic which will not be a whit inferior to the classical one for beauty of conception and internal harmony of logic. Similarly by omitting the postulate of parallelism a system of bounded geometry can be constructed so as to produce a logically self-consistent conceptual scheme. And these two conceptual schemes of bounded arithmetic and bounded geometry will possess an additional merit of being closer to the reality of our senses than the unbounded ones which, being sanctified by custom, are suffered to exist. Now it is none of the business of the mathematician to enquire whether or no his logically self-consistent conceptual scheme possesses also the attribute of applicability to physical phenomena. It is the business of the physicist. For though undoubtedly the science of mathematics owes its origin to and looks upon the problems of physical sciences as sources of inspiration, the mathematician refuses to confine himself to the limits of the problems set by the physicist. These problems often give rise to a host of other questions for which his intellectual curiosity forces the mathematician to find answers and this need of his intellectual craving leads him far beyond the original domains in which these problems arise; and in this way the mathematician produces an abstract conceptual scheme which is subject to no other test except that of logical coherence. The most abstract branches of modern mathematics such as the theory of functions of real and complex variables, the theory of differential equations had their genesis in problems of physics.\* Moreover the mathematician does not take the utilitarian view of his science as the physicist does. With him the motto is Mathematics for Mathematics' sake. Indeed it would be very instructive to compare the attitude of the physicist and the mathematician towards mathematics. But I do not hold that this is the proper place for it. Therefore, for the present, suffice it to say that the utilitarian view of any science, apart from the fact that it strangles the progress of that science, is not an absolute test, for the standard of what constitutes utility is a *function* of time. The study of conic sections originated in the practical problem of doubling the altar. But had the Greek geometers taken the utilitarian view of the subject and had they not been goaded by their intellectual curiosity to study conic sections as an abstract science, Kepler could not have been able to formulate his famous trio of laws that govern the motion of the planets in the solar system. And but for Kepler there would not have been any Newton and but for Newton there would not have been any Einstein. Similarly G. F. B. Riemann (1826-1866) hardly dreamt

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\* See *Essays in Mathematics* No. 1, §§12-16 where I have historically traced the growth of the present concept of function.

that his absolute differential calculus would one day become the vehicle for Einstein's theory of Relativity.

### 5. *Concept of Infinity a Mathematical Necessity*

In the preceding paragraphs I have endeavoured to show that the concept of infinity has neither a physical foundation nor a logical basis. Then what is it that lies behind this concept? The concept of infinity is neither an experiential nor a logical necessity, it is a mathematical necessity, a being owing its birth to the creative imagination of the mathematician who is endowed with that power of mind which is capable of conceiving the indefinite repetition of an act when this act is but once possible. The condemnation of this concept in the name of reality "would reduce mathematics to the bounded arithmetic and the bounded geometry . . . . What is valid seems so insignificant that it may be seriously doubted whether analysis is at all possible. The lofty structure erected by the mathematicians of the last three centuries must be razed to the foundation; the principles and methods which derived their power from the use of the infinite must be scrapped, the physical sciences which have so confidently applied the concepts of limit and function and number in formulating and analyzing their problems must turn over a new leaf, they must rebuild their foundations and devise new instruments in lieu of those condemned "

### 6. *The Infinite, Potential and Actual or Dynamic and Static*

Our present concept of the infinite rests on a fundamental assumption of arithmetic, *viz.* the process of counting cannot conceivably be terminated. In other words the sequence of natural numbers 1,2,3, . . . does not possess the last number, each number has a successor or there is an infinity of positive integers. Or again, if we consider  $n$  to be a positive integer, the phrase  $n$  tends to infinity is a short-hand way of saying that given a positive number  $\Delta$ , however large,  $n$  assumes values that exceed and remain greater than  $\Delta$ . This traditional concept of the infinite as a *variable* finite magnitude that grows indefinitely is often called the concept of the potential infinite in contradistinction to that of the actual infinite which is a *fixed, constant* quantity lying beyond all finite magnitudes. This concept of the actually infinite is not of recent origin. The celebrated analysts K. F. Gauss (1777-1855) and A. L. Cauchy (1789-1857) raised their protesting voice against the use of the actual infinite in mathematics. In his letter written to Schumacher in 1831 Gauss writes. "As to your proof, I must protest most vehemently against your use of the infinite as something consummated as this is never permitted in mathematics." The infinite is but a *façon de parler*; "an abridged form of the statement that limits



exist which certain ratios may approach as closely as we desire, while other magnitudes may be permitted to grow beyond all bounds." It required the courage of G. Cantor (1845-1918) to defy old traditions and "deal with the actually infinite as with a definite mathematical being." In his essay *On Linear Aggregates*, published in 1883 Cantor writes "It is traditional to regard the infinite as indefinitely growing . . . As against this I conceive the infinite in the definite form of something consummated, something capable not only of mathematical formulations, but of definition by number. This concept of the infinite is opposed to traditions which have grown dear to me, and it is much against my own will that I have been forced to accept this view. But many years of scientific speculation and trial point to these conclusions as to a logical necessity, and for this reason I am confident that no valid objections will be raised which I shall not be in a position to meet."

### 7. *The Transfinite Arithmetic*

The creative imagination of Cantor did not remain content with conceiving the infinite as capable of definition by number, it impelled him to evolve a system of comparing infinities. By introducing the concept of cardinal numbers we are able to compare two finite collections and say that they are equal or one is smaller than the other. Similarly by introducing the concept of power of an infinite aggregate Cantor is able to compare two infinite aggregates. These powers, which enable us to classify infinities just as the finite numbers 1, 2, 3, . . . enable us to classify finite collections, are known as transfinite numbers. By defining the operations of addition, multiplication and potentiation upon these transfinite numbers Cantor created a transfinite Arithmetic, an arithmetic of the infinite.

### 8 *Common sense and the Infinite*

But it must be remembered that certain fundamental *Common-sense* laws, which we find hold good in finite arithmetic, do no longer remain true if we transfer them to transfinite arithmetic, for in considering infinities we are really traversing a region that lies beyond the realm of common sense, and further, many a time in mathematics common sense has proved to be the greatest non-sense. While we are dealing with finite collections common sense tells us that a part is less than the whole. But in comparing infinities the fundamental rule is: The part *can* equal the whole, the part *may* have the power of the whole. For example, the two aggregates formed by the natural sequence and the odd integers are both infinite and the latter is a part of the former, yet it can be proved that both the aggregates have the same power. On the other hand, though the domain of rational numbers forms a part of the arithmetic continuum, the continuum is un-  
 . . .

tier than the domain of rational numbers; the power of the latter is greater than that of the former.

### 9. *Concept Craves Clarification*

The purpose of this article does not justify me in going into more details regarding the transfinite arithmetic; and I propose to conclude this essay by briefly indicating the present position concerning the concept of the infinite. The legitimacy of Cantor's use of the actually infinite in mathematics, the logical validity of his processes and the deductions drawn thereby have been put to searching criticism by leading mathematician-philosophers of the day. Among them Burali-Forti, Bertrand Russell, König and Richard are prominent; and their discussions have given rise to paradoxes and antinomies that are either logical or linguistic. As stated above Cantor said, "No valid objections will be raised which I shall not be in a position to meet." Well; the Cantorians have not only failed to meet these valid objections and to convert all mathematician-philosophers to their point of view, but on the contrary, some of the Cantorians such as F. P. Ramsey (1903-1930) are being converted to a finitist view which rejects the concept of the actually infinite. In his address in memory of K. Weierstrass, one of the greatest exponents of the movement known as arithmetization of mathematics, D. Hilbert says. "The infinite! No other question has ever moved so profoundly the spirit of man; no other idea has so fruitfully stimulated his intellect; yet no other concept stands in greater need of clarification than that of the infinite."

## NOTE ON CONFOCAL CONICS AND CONFOCAL QUADRICS

By

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I think that the following method of obtaining the equation to the system of conics or quadrics confocal with a conic or quadric given by the most general equation of the second degree has not received the attention it deserves

1. Notation Let  $s \equiv (a, b, c, f, g, h)(x, y, z)^2 = 0$  be the given conic.  $s$  may be conveniently replaced by unity.

$$\text{Let } 2\xi \equiv \frac{\partial s}{\partial x}, 2\eta \equiv \frac{\partial s}{\partial y}, \text{ and } 2\zeta \equiv \frac{\partial s}{\partial z}.$$

The envelope equation to the given conic  $s = 0$  is

$S \equiv (A, B, C, F, G, H)(X, Y, Z)^2 = 0$  where  $A, B$  etc., have the usual meanings and  $X, Y, Z$  are line co-ordinates

The circular points at infinity are given by

$$\Omega \equiv X^2 + Y^2 = 0$$

2. I will first prove that the equation

$$\begin{vmatrix} a + \lambda & h & \xi \\ h & b + \lambda & \eta \\ \xi & \eta & s \end{vmatrix} = 0$$

gives us the family of conics confocal with the given conic  $s = 0$ ,  $\lambda$  being the parameter of the family.

We know that the four vertices of the quadrilateral formed by the two pairs of tangents that can be drawn from the circular points at infinity to the conic  $s = 0$  give us the four foci of  $s = 0$ . Since the equation  $S + k\Omega = 0$ , where  $k$  is any arbitrary constant, gives us the family of conics touching the common tangents of  $S = 0$  and  $\Omega = 0$ , and further, since  $\Omega = 0$  gives us the circular points at infinity, it follows that the family of conics given by  $S + k\Omega = 0$  has the same foci as those of  $S = 0$ . In other words  $S + k\Omega = 0$  is the envelope equation to the family of conics confocal with  $s = 0$ . Now we know that the locus equation to the said family is found to be

$$\sigma \equiv \begin{vmatrix} A+h & H & G & x \\ H & B+h & F & y \\ G & F & C & z \\ x & y & z & 0 \end{vmatrix} = 0$$

Multiplying both sides of  $\sigma = 0$  by  $\delta \equiv \begin{vmatrix} a & h & g & 0 \\ h & b & f & 0 \\ g & f & c & 0 \\ 0 & 0 & 0 & 1 \end{vmatrix}$  we get

$$\sigma \cdot \delta \equiv \begin{vmatrix} \delta + ak & hk & gk & x \\ hk & \delta + bk & fk & y \\ 0 & 0 & \delta & z \\ \xi & \eta & \zeta & 0 \end{vmatrix} = 0^*$$

Multiplying the columns of the last determinant by  $x, y, z$  and  $-\delta$  respectively, and adding the results for the fourth new column, we get

$$\sigma \equiv \begin{vmatrix} a + \delta/k & h & \xi \\ h & b + \delta/k & \eta \\ \xi & \eta & s \end{vmatrix} = 0$$

Setting  $\delta/k = \lambda$ , we get the desired result.

3. The same method holds true *mutatis mutandis* in three dimensions. Let the quadric be given by

$$s \equiv (a, b, c, d, f, g, h, u, v, w) (x, y, z, t)^3 = 0$$

where  $t$  may be conveniently replaced by unity. The envelope equation of the quadric  $s = 0$  is

$$S \equiv (A, B, C, D, F, G, H, U, V, W) (X, Y, Z, T)^3 = 0.$$

The circle at infinity is represented by the equation

$$Q \equiv X^2 + Y^2 + Z^2 = 0$$

We now know that  $S + hQ = 0$  is the envelope equation to the family of quadrics confocal with the quadric  $S = 0$ . Proceeding as before, the locus equation to the said family is found to be

\* This equation may be written as

$$\delta s - h\Gamma + k^3 = 0$$

where  $\Gamma \equiv C(x^2 + y^2) - 2Gx - 2Fy + A + B = 0$  gives us the director circle of the conic  $s = 0$ ,

$$\begin{vmatrix} a + \lambda & h & g & \xi \\ h & b + \lambda & f & \eta \\ g & f & c + \lambda & \zeta \\ \xi & \eta & \zeta & s \end{vmatrix} = 0$$

where  $2\xi = \frac{\partial s}{\partial x}$ ,  $2\eta = \frac{\partial s}{\partial y}$ ,  $2\zeta = \frac{\partial s}{\partial z}$  and  $\lambda = \delta/h$

$\delta$  being the determinant  $| a \ b \ c \ d |$ .

# A NOTE ON THE AREA OF A POLYGON

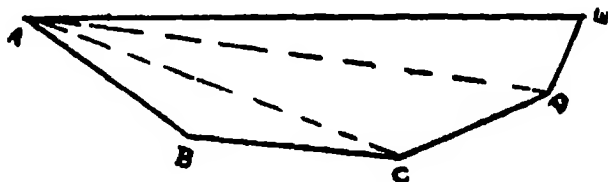
By

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This note contains an alternative proof of the following theorem. It is neat and elegant and is calculated to stimulate interest in the study of methods of Vector Analysis.

We shall prove the theorem, in the first instance, with respect to the polygon A B C D E.



Let us denote the vectors  $\overline{AB}$ ,  $\overline{BC}$ , ...,  $\overline{EA}$  by  $\alpha$ ,  $\beta$ , ...,  $\epsilon$ ; their lengths by  $a$ ,  $b$ , ...  $\epsilon$ ; the angle which  $\beta$  makes with  $\alpha$  by  $\alpha\beta$  and the unit vector normal to the plane of the polygon, by  $\nu$ . Join AC, AD.

$$\text{Then } 2\nu \Delta ABC = \overline{AB} \times \overline{AC} = \alpha \times (\alpha + \beta) = \alpha \times \beta.$$

$$\text{Similarly } 2\nu \Delta ACD = (\alpha + \beta) \times \gamma.$$

$$2\nu \Delta ADE = (\alpha + \beta + \gamma) \times \delta.$$

$$\text{Also } 0 = (\alpha + \beta + \gamma + \delta) \times \epsilon$$

$$\begin{aligned} \text{Hence } 2\nu \times \text{Polygon ABCDE} &= \Sigma \alpha \times \beta \\ &= 2\nu \Sigma ab \sin \alpha\beta \end{aligned}$$

where the sum includes all terms corresponding to combinations of  $\alpha, \beta, \dots$  taken two at a time and where the alphabetical order of factors is maintained in each term.

$$\text{Hence Polygon ABCDE} = \Sigma ab \sin \alpha\beta.$$

The foregoing method can be extended to any polygon.

c. f. Hobson's Trigonometry §129.

Also Bagi's Plane Trigonometry §131.

# SOME POINTS ABOUT ORDINARY LINEAR DIFFERENTIAL EQUATIONS

By

G. S. DIWAN

## (i) Operational Factors.

In solving ordinary linear differential equations of the second order by the method of operational factors, the following proposition is useful —

If the operator  $P_0 D^2 + P_1 D + P_2$ , in the linear differential equation  $P_0 \frac{d^2 y}{dx^2} + P_1 \frac{dy}{dx} + P_2 y = X$  is *algebraically* equivalent to  $(\alpha D + a)(bD + \beta)$ , and if  $b$  and  $\beta$  are constants (i.e., do not involve  $x$ ), then even *operationally*  $P_0 D^2 + P_1 D + P_2$  is equivalent to  $(\alpha D + a)(bD + \beta)$ , the two operational factors appearing in this very *specifio* order ( $D \equiv \frac{d}{dx}$ ).

Proof — If  $P_0 D^2 + P_1 D + P_2 \equiv (\alpha D + a)(bD + \beta)$  *algebraically*, then  $P_0 \equiv ab$ ,  $P_1 \equiv a\beta + b\alpha$ , and  $P_2 \equiv a\beta$ . The operator  $(\alpha D + a)(bD + \beta)$  operating on  $y$  gives the result  $(\alpha D + a)(b \frac{dy}{dx} + \beta y)$ , i.e.,  $ab \frac{d^2 y}{dx^2} + \frac{dy}{dx}(ab' + a\beta + b\alpha) + (a\beta + a\beta')y$  [ $b' = \frac{db}{dx}$  and  $\beta' = \frac{d\beta}{dx}$ ].  $(\alpha D + a)(bD + \beta)$  is, therefore, operationally equivalent to, say,  $Q_0 D^2 + Q_1 D + Q_2$ , where  $Q_0 \equiv ab$ ,  $Q_1 \equiv a\beta + b\alpha + ab'$ , and  $Q_2 \equiv a\beta + a\beta'$ .  $(\alpha D + a)(bD + \beta)$  will, therefore, algebraically and operationally be equivalent to the same expression if  $P_0 \equiv Q_0$ ,  $P_1 \equiv Q_1$ , and  $P_2 \equiv Q_2$ , i.e., if  $ab'$  and  $a\beta'$  are each equal to zero, which is seen to be true when  $b$  and  $\beta$  are constant quantities.

It can also be seen that under no other circumstances are the algebraical and the operational factors of  $P_0 D^2 + P_1 D + P_2$  just the same.

## (ii) Particular Integral.

[It is thought that the following notes will make some points of the theory of the particular integral of an ordinary linear differential equation clearer.]

(A) The particular integral of the ordinary linear differential

$$\text{equation } p_0 \frac{d^n y}{dx^n} + p_1 \frac{d^{n-1} y}{dx^{n-1}} + p_2 \frac{d^{n-2} y}{dx^{n-2}} + \dots + p_{n-1} \frac{dy}{dx} + p_n y = X$$

can be *uniquely* defined as that solution of the above differential equation which does not involve as part of itself any non zero value of the Complementary Function (C F) which equated to  $y$  forms the general solution of  $p_0 \frac{d^2 y}{dx^2} + p_1 \frac{d^2 y}{dx^2} + p_2 \frac{d^2 y}{dx^2} + \dots + p_n \frac{dy}{dx} + p_{n+1} y = 0$ .

[ If the two equations above are written as  $f(D)y = X$  and  $f(D)y = 0$ , then it is seen that if  $u$  and  $v$  are if possible, two particular integrals (as defined above) of  $f(D)y = X$   $f(D)u = f(D)v = X$ , and, therefore,  $f(D)(u - v) = 0$   $y = u - v$  therefore, is a solution of  $f(D)y = 0$   $u - v$  is thus a value of the C F which equated to  $y$  forms the general solution of  $f(D)y = 0$  Since neither  $u$  nor  $v$  can contain as part of itself any non zero value of the C F, by the definition as stated above, it follows that  $u - v$  must be the zero value of the C F  $u$ , therefore, must be identically the same as  $v$ , i.e. with the above definition there can be only one particular integral for a given ordinary linear differential equation ]

(B) If the particular integral of  $f(D)y = X$  is, as usual, denoted by  $\frac{1}{f(D)}X$  by defining the result of an inverse operation in the appropriate manner, then with the definition given in (A), it shall have to be understood that the result  $\frac{1}{f(D)}X$  is not to involve as part of itself any non zero value of the C F which equated to  $y$  is the general solution of  $f(D)y = 0$  The value of the result  $\frac{1}{f(D)}f(D)X$  will, therefore, strictly be *not always*  $X$ , but in every case  $X - X'$ , say, where  $X'$  is either the *whole* of the non zero value, if any, of the C F contained as part in  $X$ , or else zero if there is no such non zero value contained in  $X$  (This statement can be formally established as follows — Let  $\frac{1}{f(D)}f(D)X = u$ , say then  $f(D)u = f(D)X$ , i.e.,  $f(D)(u - X) = 0$   $u - X$ , therefore, is a value of the C F  $u$  by definition cannot contain a non zero value of the C F If  $X$  also does not contain any such non zero value of the C F, then  $u - X = 0$ , or  $u = X - X'$  where  $X'$  is zero If  $X$  does contain a non zero value  $X'$ , say, of the C F, and no other such non zero value then  $u - X = -X'$  i.e.  $u = X - X'$  where  $X'$  is the *whole* of the non zero value of the C F contained in  $X$ ) In §60 of the sixth chapter of Murray's Differential Equations the result  $\frac{1}{f(D)}e^{ax} = \frac{e^{ax}}{f(a)}$  is established as valid when  $f(a) \neq 0$  If the result is thus not valid when  $f(a) = 0$ , the process leading to the result must also at some stage or the other not be



applicable when  $f(\alpha) = 0$ . It will probably help the clear understanding of the point if it is noted that the step  $\frac{1}{f(D)} f(D) e^{\alpha x} = \frac{1}{f(D)} f(\alpha) e^{\alpha x}$  in the process leading to the result reduces to the identity  $0=0$  when  $f(\alpha) = 0$  ( $e^{\alpha x}$  being a non-zero value of the C.F. in this case), and thus fails to give any result in the exceptional case when  $f(\alpha) = 0$ .

(C) With the special meaning assigned in (B) to the result of an inverse operation as denoting a particular integral, it follows that if  $\Psi(D)$  and  $f(D)$  are operators operating on  $y$  in ordinary linear differential equations with constant coefficients, then  $\Psi(D) \frac{1}{f(D)} X = \frac{1}{f(D)} \Psi(D) X$  only if the expression on the left side does not involve as part of it any non-zero value of the C.F. corresponding to the equation  $f(D) y = 0$ . There are cases in which such a non-zero value of the C.F. is involved as part in the left side. Consider, for instance,  $D \frac{1}{D^2+1} \cos x$ , which is equal to  $\frac{\sin x}{2} + \frac{x \cos x}{2}$ . This value involves as part of itself the term  $\frac{\sin x}{2}$ , which is a non-zero value of the C.F. corresponding to the equation  $(D^2+1) y = 0$ .  $\frac{1}{D^2+1} D \cos x = -\frac{1}{D^2+1} \sin x = \frac{x \cos x}{2}$ . So it is seen in this case that  $D \frac{1}{D^2+1} \cos x \neq \frac{1}{D^2+1} D \cos x$ , for the left side contains as its part some non-zero value of the C.F. corresponding to  $(D^2+1) y = 0$ .

In §64 of the sixth chapter of Murray's Differential Equations the formula  $\frac{1}{f(D)} x V = x \frac{1}{f(D)} V - \frac{1}{f(D)} f'(D) \frac{1}{f(D)} V$  is deduced. The last term on the right side of this formula is often taken as  $-f'(D) \frac{1}{[f(D)]^2} V$  or as  $-\frac{1}{[f(D)]^2} f'(D) V$ . We may call these two modifications of the formula modifications ( $\alpha$ ) and ( $\beta$ ) respectively. It will now be seen that such a modification is not always correct as the direct operator  $f'(D)$  and the inverse operator  $\frac{1}{f(D)}$  are not always commutative. Where such a modification is not correct, the use of the formula in either of the forms ( $\alpha$ ) or ( $\beta$ ) instead of in the original form (which is always correct) leads to an error. Such a case practically arises when  $f(D)$  is a power of

\* See Johnson's *Treatise on Differential Equations* (3rd edition), page 112.

$(D^2+a^2)$  and  $V$  is the trigonometric function  $\cos ax$  or  $\sin ax$ . In the footnote given on page 123 of the third edition of Johnson's treatise on Differential Equations, it is said that in cases analogous to the evaluation of  $\frac{1}{D^2+a^2} x \cos ax$ , the method that 'should always be employed' is to consider  $\frac{1}{D^2+a^2} x \cos ax$  as the real part in  $\frac{1}{D^2+a^2} x e^{ax}$ ; and that 'an error might arise' if the method of §64 in Murray's book is used. In this connection it is to be noted that the error arises *only* if form (a) or (β) of the formula (both of which forms are as shown above incorrect in such cases) is used, and the formula in its *original* form gives correctly the value of a particular integral of the type  $\frac{1}{(D^2+a^2)^r} x^s V$ , where  $r$  and  $s$  are positive integers and  $V = \cos ax$  or  $\sin ax$ . To illustrate the point the result  $\frac{1}{D^2+a^2} x \cos ax$  is worked out in full below:—

$$\begin{aligned} \frac{1}{D^2+a^2} x \cos ax &= x \cdot \frac{1}{D^2+a^2} \cos ax - \frac{1}{D^2+a^2} 2D \frac{1}{D^2+a^2} \cos ax \\ &= x \cdot \frac{x \sin ax}{2a} - \frac{1}{D^2+a^2} 2 \cdot \frac{1}{2a} (\sin ax + ax \cos ax) \\ &= \frac{x^2 \sin ax}{2a} - \frac{1}{D^2+a^2} x \cos ax - \frac{1}{a} \cdot \frac{1}{D^2+a^2} \sin ax \\ \therefore \frac{2}{D^2+a^2} x \cos ax &= \frac{x^2 \sin ax}{2a} + \frac{x \cos ax}{2a^2}, \text{ i. e.,} \\ \frac{1}{D^2+a^2} x \cos ax &= \frac{x^2 \sin ax}{4a} + \frac{x \cos ax}{4a^2}. \end{aligned}$$

Had the modified form (a) been incorrectly used to evaluate the particular integral, the result would have been  $\frac{x^2 \sin ax}{4a} + \frac{x \cos ax}{2a^2}$ , and if form (β) were used the result would be merely  $\frac{x^2 \sin ax}{4a}$ .

It should also be remarked that though  $x \cos ax = -2a \cdot \frac{1}{D^2+a^2} \sin ax$ , still  $\frac{1}{D^2+a^2} x \cos ax$  is not  $= -2a \frac{1}{(D^2+a^2)^2} \sin ax$ , which latter is seen to be equivalent to  $\frac{x^2 \sin ax}{4a}$ . The reason for this non-equivalence is that  $\frac{1}{f(D)}$  [the function of  $x$  given by  $\frac{1}{f(D)}X$ ] is

equal to  $\frac{1}{[f(D)]^2} X$  only if the former does not involve a non-zero value of the C. F. corresponding to the equation  $[f(D)]^2 y = 0$ .

If the second term on the right side of the modified form ( $\alpha$ ) is taken as  $-f'(D) \frac{1}{f(D)} \left[ \frac{1}{f(D)} V \right]$ , then the value of the particular integral so obtained in the exceptional cases indicated above will not in itself be incorrect but will be involving some non-zero value of the C.F. Such a method, however, is not practical; since in the evaluation of  $\frac{1}{f(D)} \left[ \frac{1}{f(D)} V \right]$  where, say,  $V = \cos ax$  and  $f(D) = (D^2 + a^2)$ , the use of the original form of the formula in §64 of Murray's book appears to be necessary. Similarly if the modified form ( $\beta$ ) is taken with the second term on the right side as  $-\frac{1}{f(D)} \left[ \frac{1}{f(D)} f'(D) V \right]$  then the value of the particular integral so obtained in the exceptional cases will be incorrect.

## A NOTE ON THE PROPER NOMENCLATURE FOR "VRAIE VALEUR"

By

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If a functional form  $f(x)$  becomes indeterminate for a value  $x = a$ , but limit  $f(x)$  as  $x \rightarrow a$  exists, Vallée Poussin calls the limit "*Vraie Valeur*" of the function at  $x = a$  (Cours d'Analyse, Vol. I, §82). This has been translated into English as "*true value*" by Gibson (*Elementary Treatise on the Calculus*, p. 418) and Mahajan's (*Lessons in Analysis*, p. 70).

It seems that the term "*Vraie Valeur*" or "*true value*" is unfortunate and somewhat misleading. Other terms which would be less objectionable may be suggested, such as "*natural value*" or "*appropriate value*" or "*fitting value*". Personally I consider "*appropriate value*" as the most natural, appropriate and fitting and would recommend it for general adoption.

# A NOTE ON THE GENERAL EQUATION OF THE SECOND DEGREE WHEN IT REPRESENTS TWO PLANES

By

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In ex. 8 page 34 of Bell's Solid Geometry the condition that the General Equation  $ax^2 + by^2 + cz^2 + 2fyz + 2gax + 2hxy = 0$ , represents two planes is mentioned and the student is at a loss to understand why the more general case of  $ax^2 + by^2 + cz^2 + 2fyz + 2gax + 2hxy + 2ux + 2vy + 2wz + d = 0$  when it represents two planes should not be discussed. No doubt the discussion has its place in Chapter XI; but the method involved is longer and cannot be picked up easily in the earlier stages.

Bell mentions the conditions on page 217 of his book but these are not explicit. An attempt is made here to express these conditions and to deduce them from very elementary considerations without the help of much mathematical analysis.

As shown by Bell the conditions practically reduce to those required for the four planes.

$$\begin{aligned} ax + hy + gz + u &= 0 \\ hx + by + fz + v &= 0 \\ gx + fy + cz + w &= 0 \\ ux + vy + wz + d &= 0 \end{aligned}$$

to pass through one and the same st. line.

Hence these may be written as.—

$$(i) \begin{vmatrix} a & h & g & u \\ h & b & f & v \\ g & f & c & w \\ u & v & w & d \end{vmatrix} = 0 \quad (ii) \begin{vmatrix} a & h & g & u \\ h & b & f & v \\ u & v & w & d \end{vmatrix} = 0$$

The first of these is equivalent to any two of four determinants being equal to zero, which may be written as  $D=0$ ,  $K_1=0$ ,  $K_2=0$ ,  $K_3=0$  where

$$D = \begin{vmatrix} a & h & g \\ h & b & f \\ g & f & c \end{vmatrix} \quad K_1 = \begin{vmatrix} a & h & u \\ h & b & v \\ g & f & w \end{vmatrix}$$

$$K_2 = \begin{vmatrix} a & g & u \\ h & f & v \\ g & c & w \end{vmatrix} \quad K_3 = \begin{vmatrix} h & g & u \\ b & f & v \\ f & c & w \end{vmatrix}$$

If any two of these are satisfied the others are also automatically satisfied. The second is similarly equivalent to any two of the four determinants involved, viz.,

$$K_1 = 0, \Delta_1 = 0, \Delta_2 = 0, \Delta_3 = 0$$

$$\text{where } \Delta_1 = \begin{vmatrix} a & h & u \\ h & b & v \\ u & v & d \end{vmatrix} \quad \Delta_2 = \begin{vmatrix} a & g & u \\ h & f & v \\ u & w & d \end{vmatrix}$$

$$\text{and } \Delta_3 = \begin{vmatrix} h & g & u \\ b & f & v \\ v & w & d \end{vmatrix}$$

If any two of these are satisfied the others are also automatically satisfied.

Hence on the whole the conditions are equivalent to the following —

$$D = 0$$

$$\text{Any one of } K_1 = 0, K_2 = 0, K_3 = 0,$$

$$\text{Any one of } \Delta_1 = 0, \Delta_2 = 0, \Delta_3 = 0$$

It is easily seen that the conditions are equivalent to any three of the seven determinants equated to zero, viz.,

$$D, K_1, K_2, K_3, \Delta_1, \Delta_2, \Delta_3$$

and may be taken as  $\Delta_1 = 0, \Delta_2 = 0, \Delta_3 = 0$ . The others follow as a matter of analysis.

This result is easily deducible from general considerations. Any section of the two planes is two st lines. Hence if the sections by the planes  $x=0, y=0, z=0$  not passing through the same st. line are st. lines the equation must represent two planes. No other surface of the second degree has this property.

$$\therefore ax^2 + by^2 + 2hxy + 2ux + 2vy + d = 0$$

$$ax^2 + cz^2 + 2gax + 2ux + 2wz + d = 0$$

$$by^2 + cz^2 + 2fyz + 2vy + 2wz + d = 0$$

represent pairs of st. lines. Conditions for which are

$$\Delta_1 = \begin{vmatrix} a & h & u \\ h & b & v \\ u & v & d \end{vmatrix} = 0 \quad \Delta_2 = \begin{vmatrix} a & g & u \\ g & c & w \\ u & w & d \end{vmatrix} = 0$$

$$\Delta_1 = \begin{vmatrix} b & f & v \\ f & c & w \\ v & w & d \end{vmatrix} = 0$$

as previously established. As can be seen from what has been said before that  $D = 0$  automatically, and this disposes of, as a particular case, ex. 8 on page 34, referred to above.

## DESCRIPTIVE MATHEMATICS

By

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I have been asked to write a note on a new course for First Year Mathematics which it is proposed from this year to make alternative to the usual course in Algebra, Geometry and Trigonometry. It is entitled "Descriptive Mathematics", and is detailed as follows:

PAPER I.—Logarithms. The general quadratic. Graphs of  $y=x^n$  for rational values of  $n$ , and of  $y=a^x$ , with applications. Graphs of

$$y = ax^m + bx^{m-1} + cx^{m-2} + \dots + k.$$

Averages. Frequency distributions. Empirical probability. Binomial theorem for a positive integral index. Evaluation of determinants. Simple standard derivates and elementary integrals with applications.

PAPER II.—Slide scales. Similarity of triangles. Inversion. Nomograms. Graphical rulings. The determination of empirical formulæ. Graphical solution of equations. The radian. Circular functions and their graphs. Solution of triangles and simple two dimensional problems. Addition formulæ.

The suggestion to institute such a course came from the feeling that the more conventional syllabus in First Year mathematics was not fulfilling a generally useful purpose in the educational scheme. This feeling has also expressed itself in the plan for "bifurcation", under which mathematics as a subject in the First Year would no longer be compulsory, but would become merely an alternative which students who value it might choose. Teachers of mathematics share this feeling, and acquiesce in this negative solution. The ordinary course in mathematics may not be uninteresting, and it is doubtless valuable as a mental discipline to some students; but it is plain that it is not within the power of a large number of otherwise able students to profit from it to any satisfactory degree.

Yet the University of Bombay has seemed reluctant to follow the example of other Universities in adopting bifurcation of studies at so early a stage in order to avoid this danger of unprofitable drudgery. A remedy more adequate to the students' needs seems desirable, and the course in Descriptive Mathematics is an attempt to find *a more positive solution*. It is not inconsistent, however, with the proposal to "bifurcate", though the alternatives to be allowed may result in a



tendency to make the course cater for too narrow a class of student. It has to be realised that, while too frequently misuse occurs in applications of mathematical methods, the trend of all study and investigation in the modern world is such as to increase the importance of the part that mathematics plays in the search for truth. Accordingly it seems clear that a sustained effort should be made to give students as adequate an idea as possible of how mathematical devices, at least those of an elementary type, may be applied in appropriate ways to elucidate certain types of phenomena.

Thus far the investigations that have been made with this end in view have made two things abundantly clear. The first is the surprising range of *variety* often seen in the *applications* of the same mathematical tool. An example is given by equilateral-triangle rulings, sometimes called "architects' isometric paper". There are the well-known applications to three-component systems in engineering, in geology, and in chemistry, though the significance of the generalisation to multicomponent systems in the last is not so well-known. Also in physics use of the triangles is made in various ways, particularly in the study of colour. In dietetics certain properties of foods are conveniently represented on these triangles, and a distortion of the triangles makes possible a suggestive and comprehensive representation of aspects of metabolism. Equilateral triangles may be employed too in the study of types or changes in populations. Quite a different use of the same rulings is that for isometric drawings, and it has been found convenient in statistics as affording a comparatively easy means of scrutinizing and interpreting measurements of different types after regression values have been calculated.

The second result is that there is a *unity* and a development in the *mathematical principles*, on which are based those quantitative methods which are actually being applied, which constitute them a "body of knowledge" worthy to be compared with that in the more conventional mathematical course. Such a claim can be substantiated only after the new course has been fully tested in practice, but a glance at the detailed syllabus will show at least the possibility that there is actually in it something of the simplicity and the range which are aimed at in mathematical method.

It is not possible or fitting to examine here the proposed course in detail. Only some features of its relation to other branches of study may be mentioned. "Descriptive Mathematics", the title chosen to characterize the course, has a utilitarian bias. It indicates that endeavour is being made to deal with those mathematical devices which are found suitable for the description of quantitative phenomena or methods in different sciences. But signs are plentiful enough that what is emerging possesses considerable *cultural value*, not only for the student

who will turn to other studies with the knowledge that mathematics is more than an intricate system of abstractions and manipulations, but even for the student of mathematics who presumably has profited most from the ordinary course. After all, the ordinary course is but a continuation of the type of mathematics usually taught in schools, and it seems a deprivation further to confine the mathematical activities of a student with a flair for the subject to lines of approach with which he is already thoroughly familiarized. In the new course the clever mathematical student gets glimpses of possibilities of generalization and of application which give him an opportunity to exercise his powers to the full in a way that will often be illuminating in his later studies.

It appears that one of the most useful functions the new course may help to perform for students generally is to develop *the critical attitude*. An outstanding physiologist, who has found it necessary to use mathematics somewhat extensively in his researches, says that he finds that mathematics reveals to him, not so much what he should do, but rather what lines of investigation it may be fruitless to follow. It is probably true that aid to criticism comes from mathematics mainly through the variety of its methods making possible a scrutiny appropriate to a particular occasion, and in Descriptive Mathematics emphasis is repeatedly laid on the degree of fitness of an approach to a topic. Under the ordinary course an alternative proof is often regarded as merely a happy accident, useful in the verification of what had not been already clearly apprehended. There is need to extend greatly the idea that *flexibility of method* is something of essential worth, leading to a fuller appreciation of the meaning of the subject matter. But on occasion too criticism depends on ability to manipulate, and great stress is laid in the new course on methods which make it possible to push a calculation through to a definite stage where it may be regarded in relation to the other aspects of the matter. The need for a critical attitude may be illustrated from a standard textbook, Price's "Practice of Medicine". On page 414 thereof in detailing a calculation for the diet of a diabetic patient, the instruction is given to "divide by the arbitrary figure 30". The word "arbitrary" in itself arouses suspicion; yet this textbook in its third edition has no comment on this astonishing direction it would seem almost obvious that it could have no application beyond the case of the patient under consideration. In applications of advanced mathematics it may often be that results have to be assumed without any appreciation of the way they have been obtained; but it can only lessen alertness if this attitude of acquiescence is allowed to apply to the most elementary processes. In this respect our training in mathematics should become but *an aid to common sense*. It should be mentioned that when a distinguished professor

of mathematics in the north of England had the proposed course explained to him, his first comment was, "Well, this will certainly teach the students arithmetic!" He had found that his students, even those with mathematical ability, could not be trusted to be accurate in making calculations. Probably in this respect students in India are not any more reliable, and this is a practical defect which the ordinary course in mathematics does practically nothing to remedy.

There is *much still to be done* in discovering how mathematics may be most usefully employed in economics and in the sciences generally. At present it is evident there is much teaching that could be dispensed with, were students to come to their special studies with appropriate mathematical preparation. Statistics tends to be treated as an ornament to be added to knowledge acquired, instead of as a means to critical appreciation of such knowledge. Again, workers in the different sciences respond in curiously different ways to the suggestions of this course. Many botanists hail it as a possible means of removing obstacles that have long hindered them in the presentation of important aspects of their subject, while zoologists seem to see nothing in it that is related to their needs. I am assured that this is an historical accident and that the problems of botanists and of zoologists are essentially the same, though the latter are "still very much dominated by old morphological conceptions". This variety of response to Descriptive Mathematics but confirms the anticipation that the situation the course seeks to deal with is in some respects far from being defined. It is clear, however, that teachers of mathematics who, venturing along such lines as are indicated in Descriptive Mathematics, try to help non-mathematical students of the sciences to acquire more effective methods of study will find exhilarating surprises in store for them.

# NOTE ON A METHOD OF SOLVING SPHERICAL BY PLANE TRIANGLES

By

V. B. NAIK

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Having had occasion, in the course of certain Astronomical calculations, to obtain approximate solutions of a series of spherical triangles of a particular type, I was led to consider whether a method could be devised for the purpose, graphical or geometrical, which would give the results readily and with a fair degree of accuracy, say, correct within a quarter or a half of a degree. I found in my attempts that a spherical triangle can be connected with one or more of three plane triangles of a particular type which can be readily constructed geometrically from any three given elements of the spherical triangle. The geometrical construction is greatly facilitated by the use of a graduated quadrant of a circle (of radius = 10 cm. say) drawn on squared paper (divided into sq. millimetres)

I obtained the *connection between the spherical and the plane triangles* from certain projective properties of the sphere, the kind of projection used being simple but different from those in ordinary use. It can also be obtained and proved by using the ordinary formulae of Spherical Trigonometry.

2. Let P, Q be two intersecting planes and let the plane R pass through their common section and bisect the angle between them. Let X be any point and X' its reflection in the plane R. Then

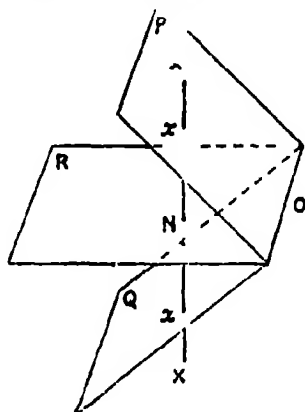


FIG. 1.

$XX'$  is bisected by the plane  $R$  at right angles. If  $XX'$  intersects the planes  $P, Q$  in  $x, x'$  respectively, we shall for our present purpose, speak of  $x, x'$  as the *equi-sectional projections of  $X$  with respect to the planes  $P, Q$* .

Given two planes  $P, Q$  and any figure  $V$  in a plane parallel to either of the planes, we can by drawing st. lines through all the points of  $V$ , perpendicular to the plane  $R$  which bisects the angle between  $P, Q$ , obtain the projections  $V'$  and  $V''$  of  $V$  on the planes  $P, Q$ . We shall speak of each of these as an *equi-sectional projection of  $V$  with respect to the planes  $P, Q$* . (We shall neither use nor have occasion to use the term in the case of a figure  $V$  not in a plane parallel to  $P$  or  $Q$ ).

3. The following simple *properties of equi-sectional projection* can be easily proved —

(i) The equi-sectional projection of any st. line is a st. line of equal length.

(ii) The angle between the equi-sectional projections of two given st. lines is equal to the angle between them.

(iii) The equi-sectional projection of any curve or any portion of a curve is equal and similar in all respects to the original.

4. In applying this projection to points and lines connected with a sphere, I shall, with a view to avoid lengthy descriptions, use in what follows the usual astronomical terms for points and lines connected with the celestial sphere.

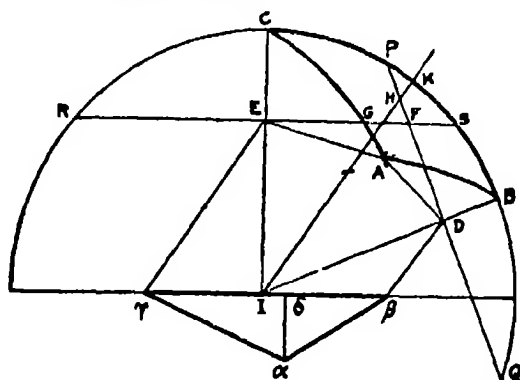


FIG 2.

On the celestial sphere of centre  $I$  and radius unity, let  $A$  be a star,  $B$  the pole and  $C$  the zenith, the arc  $BC$ , a part of the meridian, being in the plane of the paper. Let  $D, E$  be the centres of the small circles,  $PAQ$  and  $RAS$ , of which the sph. radii are the arcs  $BA, CA$  respectively and of which the diameters  $PQ, RS$  in the plane of the meridian intersect in  $F$ .

Let  $K$  be the mid-point of the arc  $BC$ , so that  $IK$  bisects  $\angle BIC$ . Then in projecting equi sectionally with respect to the planes of the horizon and the equator we have to draw two st. lines parl. to  $IK$ . The projections on the plane of the horizon are shown in the figure as they would appear when that plane is rotated about the north south line until it coincides with the plane of the paper.

Let  $\alpha, \beta, \gamma, \delta$  denote the projections of  $A, D, E, F$ .

Then, in the  $\Delta \alpha\beta\gamma$ ,

$$\alpha\gamma = AE = ES, \quad \alpha\beta = AD = DP,$$

$$\angle \gamma = \angle AEF, \quad \angle \beta = \angle ADF,$$

$$\text{and since } \angle AFE = 90^\circ, \therefore \alpha\delta \text{ is perp. to } \beta\gamma$$

5. Now,  $A, B, C$  and  $\alpha, \beta, \gamma$  being the angles and sides of the spherical triangle  $ABC$ , the angles and sides of the plane triangle  $\alpha\beta\gamma$  are connected with them by relations which are obtained as follows.—

$$\angle \beta = \angle ADP = \angle B, \text{ (i)}, \quad \angle \gamma = \angle AES = \angle C, \text{ (ii)},$$

$$\gamma\alpha = AE = \sin CIA = \sin b, \text{ (iii)},$$

$$\beta\alpha = AD = \sin DIA = \sin c, \text{ (iv)}.$$

$$\text{Also, } I\gamma = IE \tan IE\gamma = \cos b \tan \frac{\alpha}{2}, \text{ (v)};$$

$$I\beta = ID \sin ID\beta / \sin D\beta I$$

$$= \cos PID \sin BIK / \cos CIK = \cos c \tan \frac{\alpha}{2}, \text{ (vi)};$$

$$\text{whence,} \quad \beta\gamma = (\cos b + \cos c) \tan \frac{\alpha}{2} \quad \dots \dots \dots \text{(A)}$$

6. The diameters  $PQ, RS$  of the small circles  $PAQ, RAS$  intersect in  $F$ . Let  $IK$  intersect  $RS$  in  $G$  and  $PQ$  in  $H$ .

Then, the equi-sectional projection of  $AF$  is  $\alpha\delta$ ,

and  $\alpha\delta$  is perp. to  $\beta\gamma$ .

Also, the  $\Delta FGH$  is isosceles, so that

$$\angle HGF = \angle GHF = 90^\circ - \frac{\alpha}{2}, \text{ and } GH = 2 FG \sin \frac{\alpha}{2}.$$

$$\text{Now, } GH = IH - IG = (ID - IE) \sec \frac{\alpha}{2} = (\cos c - \cos b) \sec \frac{\alpha}{2},$$

$$\therefore FG \sin \alpha = 2 FG \sin \frac{\alpha}{2} \cos \frac{\alpha}{2} = GH \cos \frac{\alpha}{2} = \cos c - \cos b.$$

But  $FG$  projects into  $I\delta$  equi-sectionally,

$$\therefore I\delta \sin \alpha = \cos c - \cos b \quad \dots \dots \dots \text{(B)}$$

7. Again,

$$\begin{aligned} I\delta (1 - \cos \alpha) &= I\delta \sin \alpha \tan \frac{\alpha}{2} = (\cos c - \cos b) \tan \frac{\alpha}{2} \\ &= I\beta - I\gamma, \text{ by (v) and (vi)} \end{aligned}$$

$$\begin{aligned}\therefore I\delta (1 + \cos a) &= 2 I\delta - I\delta (1 - \cos a) = 2 I\delta - I\beta + I\gamma \\ &= (I\gamma + I\delta) - (I\beta - I\delta) \\ &= \gamma\delta - \beta\delta.\end{aligned}$$

$\therefore$  From B, by division, we get

$$(\gamma\delta - \beta\delta) \tan \frac{a}{2} = \cos c - \cos b. \quad \dots \dots (C)$$

8. The results (A), (B) and (C) proved above form the basis of the geometrical methods of solution of spherical triangles presented below. In describing the methods, to avoid confusion, I suppose that the given spherical triangle has not more than one of its given sides greater than a right angle and whenever such a side exists, I take it as the side denoted by  $a$ . It can be easily shown that this supposition does not limit the scope of application of the method. If for instance two of the given sides are each greater than a right angle, we may apply the method to the colunar triangle. The following considerations also will be of use in the application of the method.

$$\text{From (A), } \gamma\beta = (\cos b + \cos c) \tan \frac{a}{2} = \gamma I + I\beta.$$

Hence, always supposing  $\gamma\beta$  as drawn from left to right, we have.—

- if  $b < 90^\circ$  and  $c < 90^\circ$ , I lies between  $\beta$  and  $\gamma$ ,
- if  $b > 90^\circ$  and  $c < 90^\circ$ , I lies to the left of  $\gamma$ ;
- and if  $b < 90^\circ$  and  $c > 90^\circ$ , I lies to the right of  $\beta$ .

Also from (B),  $I\delta \sin a = \cos c - \cos b$

Hence,  $I\delta$  being supposed positive when  $\delta$  lies to the right of I, we have —

- if  $b < 90^\circ$ ,  $c < 90^\circ$  and  $b > c$ ,  $\delta$  is to the right of I;
- if  $b < 90^\circ$ ,  $c < 90^\circ$  and  $b < c$ ,  $\delta$  is to the left of I;
- if  $b > 90^\circ$ ,  $c < 90^\circ$  and  $b > c$ ,  $\delta$  is to the right of I;
- and if  $b > 90^\circ$ ,  $c > 90^\circ$  and  $b < c$ ,  $\delta$  is to the left of I;
- whence, if  $\delta$  is to the right of I,  $b > c$ ,
- and if  $\delta$  is to the left of I,  $b < c$ .

9. In making the constructions to be described, one is supposed to be provided with (besides the ordinary geometrical instruments) a *Quadrant* XOY of a circle of unit radius (= 100 mm. say) drawn on a plane surface ruled with two sets of lines respectively parallel to OX and OY. The arc XY must be graduated in degrees, and the Quadrant should be fitted with a revolving radius, (either a piece of fine thread or a straight metal edge.)

In the diagrams, the following notation is used throughout:—

$a, b, c$ , marks on XY corresponding to sides  $a, b, c$ , of  $\triangle ABC$ ;  
 $g, h$ , do, do,  $\frac{1}{2}a$  and  $\frac{1}{2}b$ ;

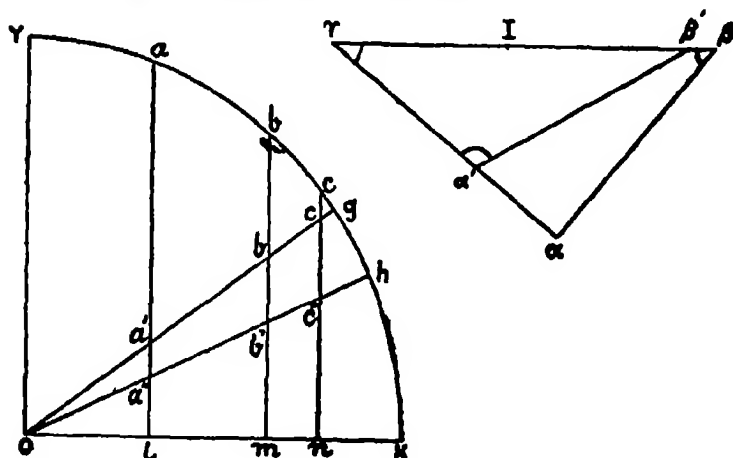
$l, m, n$ , projections of  $a, b, c$  on  $OX$ ,  
 $a', b', c'$ , } intersections of the ordinates  $al, bm, cn$  with  $Og$  and  
 $a, b, c$ , }  $Oh$  respectively

Further, we shall denote the ordinates of  $a, b, a', b'$  etc by  $(a)$ ,  $(b)$   $(a')$ ,  $(b')$ , etc, so that  $(a) = al$ ,  $(a') = a'l$ , and so on

The use of the Quadrant is essential in the constructions It is to be used for three purposes —

- (i) Noting marks on  $XY$  corresponding to given angles and vice versa
- (ii) Noting marks on  $XY$  corresponding to given projections on  $OX$
- (iii) Noting lengths of ordinates

10 Case I Given  $a, b, c$ , to find  $A, B, C$



Solution — Construct  $\Delta a\beta\gamma$ , such that

$$\beta\gamma = (b') + (c'), \gamma a = (b), a\beta = (c)$$

Also, construct  $\Delta a'\beta'\gamma$ , with  $a', \beta'$  on  $\gamma a, \gamma\beta$  respectively, such that

$$\gamma\beta' = (a), \gamma a' = (a') + (c')$$

Then,  $A = \angle \gamma a'\beta'$ ,  $B = \angle a\beta\gamma$ ,  $C = \angle \beta\gamma a$

Proof — In the  $\Delta a\beta\gamma$ ,

$$\beta\gamma = (b') + (c') = (\cos b + \cos c) \tan \frac{\alpha}{2},$$

$$\gamma a = (b) = \sin b, \text{ and } a\beta = (c) = \sin c$$

$$\therefore \text{By (A), } B = \angle a\beta\gamma, C = \angle \beta\gamma a.$$

Also, in the  $\Delta a'\beta'\gamma$ ,

$$\gamma a' = (a') + (c') = (\cos a + \cos c) \tan \frac{b}{2},$$

$$\gamma\beta' = (a) = \sin a, \text{ and } \angle \beta\gamma a = C$$

$\therefore$  By a relation similar to (A),  $A = \angle \gamma a'\beta'$ .



[ In the diagram, we have :—

Given,  $\alpha = 70^\circ 15'$ ,  $b = 49^\circ 30'$ ,  $c = 38^\circ 45'$ ,  
we find,  $A = 110^\circ 45'$ ,  $B = 49^\circ$ ,  $c = 38^\circ 30'$  ].

Case II. Given  $A, B, C$ ; to find  $a, b, c$ .

Solution.—Solve, as in Case I, the polar  $\Delta$  of  $ABC$ .

11. Case III. Given  $a, b, C$ ; to find  $A, B, c$ .

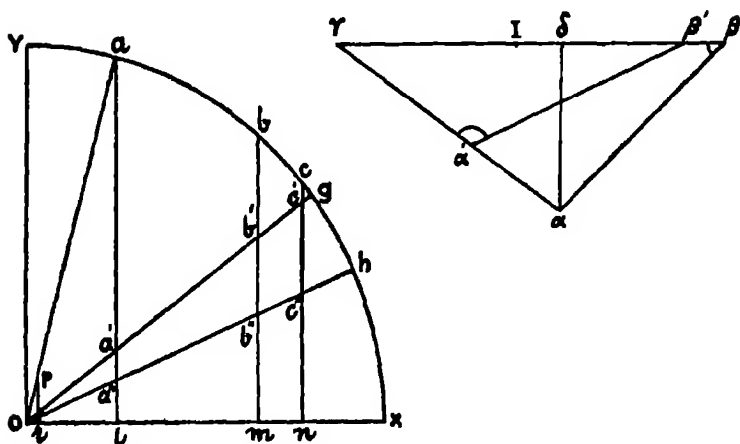


FIG 4.

Solution.—Construct  $\Delta \alpha \gamma I$ , such that

$$\angle \alpha \gamma I = C, \quad \gamma I = (b'), \quad \gamma \alpha = (b).$$

Draw  $\alpha \delta$  perp. to  $\gamma I$  produced if necessary. On  $O\alpha$  in the Quadrant, make  $O\phi = I\delta$ , and on  $OX$  mark off  $mn = (\phi)$  to the right or left of  $m$  according as  $\delta$  is to the right or left of  $I$ . Then, if  $no$  is the ordinate at  $n$  to the arc  $XY$ .

$c$  = the angle given by the graduation mark  $c$ .

Now, construct  $\Delta s \alpha \beta \gamma$  and  $\alpha' \beta' \gamma$ , by taking

$$I\beta = (c'), \quad \gamma \beta' = (\alpha), \quad \gamma \alpha' = (\alpha') + (c').$$

$$\text{Then,} \quad A = \angle \gamma \alpha' \beta', \quad B = \angle \alpha \beta \gamma.$$

$$\begin{aligned} \text{Proof.}—On &= Om + mn = Om + (\phi) \\ &= \cos b + I\delta \sin \alpha \end{aligned}$$

Hence,  $\cos c = On$ , which gives  $c$ .

Rest of the proof is the same as in Case I.

[ In the diagram, we have,

Given  $\alpha = 76^\circ 30'$ ,  $b = 50^\circ 15'$ ,  $C = 34^\circ 15'$ ;  
we find  $A = 121^\circ 30'$ ,  $B = 42^\circ$ ,  $c = 40^\circ$ . ]

Case IV. Given  $A, B, c$ , to find  $a, b, C$

Solution.—Solve as in Case III the polar triangle of  $ABC$ .

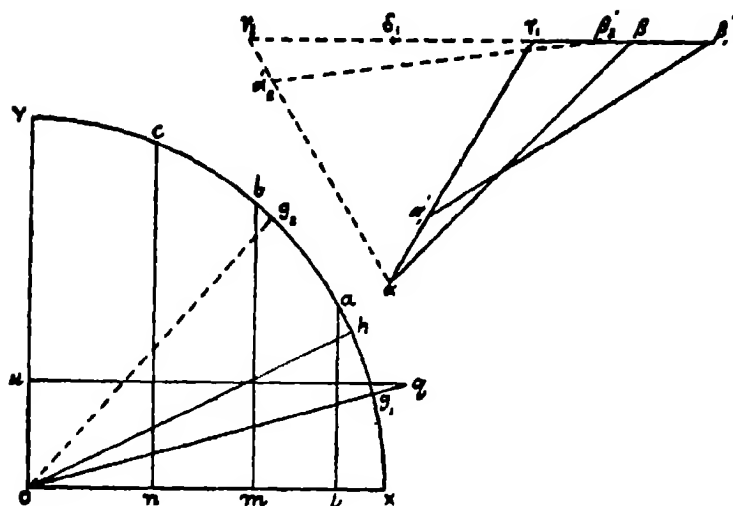


FIG. 5.

12. *Case V.* Given  $b, c, B$ , to find  $A, C, \alpha$ ; ( $c > b$ ).

*Solution* :—Construct  $\Delta \alpha \beta \gamma$ , such that

$\angle \beta = \angle B$ ,  $\alpha \beta = (c)$ ,  $\alpha \gamma = (b)$ , (ambiguous case).

Suppose we get two solutions, viz.  $\Delta s \alpha \beta \gamma_1$  and  $\alpha \beta \gamma_2$ .

Note  $u$  on  $OY$  such that  $Ou = nm$ , and note  $p, q$  on the ordinate at  $u$  such that  $up = \beta \gamma_1$  and  $uq = \beta \gamma_2$ . Note now the points  $g_1$  and  $g_2$  where  $Op$  and  $Oq$  cut arc  $XY$ . Then

$\alpha_1 = 2$  the  $\angle$  marked by  $g_1$  and  $C_1 = \angle \beta \gamma_1 \alpha$ .

Also,  $\alpha_2 = 2$  the  $\angle$  marked by  $g_2$  and  $C_2 = \angle \beta \gamma_2 \alpha$ .

To find  $A_1, A_2$ , now proceed as in case I.

*Proof* :—If  $\alpha \delta$  be perp. to  $\beta \gamma_1 \gamma_2$ , then by property (C)

$$nm = \cos b - \cos c = (\delta \beta - \gamma \delta) \tan \frac{\alpha}{2}.$$

Now  $\gamma \delta$  is +ve or -ve according as  $\delta$  lies to the right or left of  $\gamma$ ; also  $\delta \gamma_1 = \gamma, \delta$ .

$$\therefore \text{For } \Delta \alpha \beta \gamma_1, nm = (\delta \beta + \gamma \delta) \tan \frac{\alpha_1}{2} = \gamma_1 \beta \tan \frac{\alpha_1}{2}.$$

$$\text{and for } \Delta \alpha \beta \gamma_2, nm = (\delta \beta - \gamma \delta) \tan \frac{\alpha_2}{2} = \gamma_1 \beta \tan \frac{\alpha_2}{2}.$$

$$\therefore \tan \frac{\alpha_1}{2} = \frac{nm}{\gamma_1 \beta} = \frac{Ou}{uq} = \tan g_1; \tan \frac{\alpha_2}{2} = \frac{nm}{\gamma_1 \beta} = \frac{Ou}{up} = \tan g_2.$$

Hence the given construction for  $\alpha_1$  and  $\alpha_2$ .

[ In the diagram we have

Given  $b = 50^{\circ} 45'$ ,  $c = 69^{\circ} 15'$ ,  $B = 44^{\circ} 30'$ ;  
 we find  $A_1 = 25^{\circ} 45'$ ,  $C_1 = 122^{\circ} 30'$ ,  $a_1 = 29^{\circ} 0'$   
 $A_2 = 115^{\circ} 30'$ ,  $C_2 = 57^{\circ} 30'$ ,  $a_2 = 95^{\circ} 15'$  ].

*Case VI.* Given  $B, C, b$ ; to find  $a, c, A$ .

*Solution* :—Solve as in case V the polar  $\Delta$  of  $ABC$ .

The formulae (A), (B), (C) may be used to derive the usual fundamental formulae of Spherical Trigonometry; also proofs of the geometrical constructions given above may be obtained by using the ordinary formulae, but are somewhat lengthy and unnecessary here.

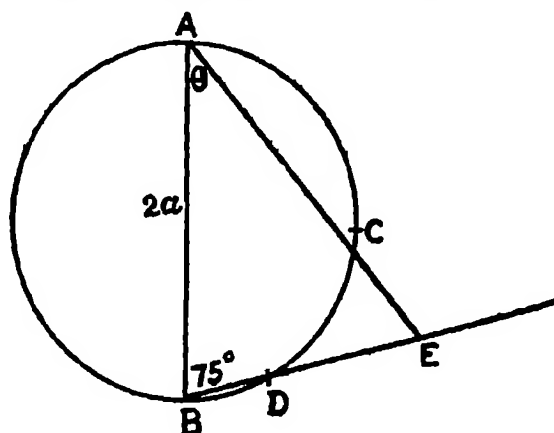
# AN APPROXIMATE CONSTRUCTION FOR AN ANGLE OF $40^\circ$

By

V. M. TELANG, B. A.

The following very elegant and simple method of approximately constructing an angle of  $40^\circ$  is given by me in the Indian Mathematical Society's Magazine, January, 1933.

Take a circle ABC. AB is the diameter and C the midpoint of Arc AB. With centre C and radius  $= \frac{1}{2}$  AB cut arc CB at D. Join



BD and measure BE = BC. Then the angle BAE = approx.  $40^\circ$ .

For let AB =  $2a$ , then BC =  $a\sqrt{2}$  and the angle ABD =  $75^\circ$ . Hence if  $\angle$  BAE =  $\theta$ .

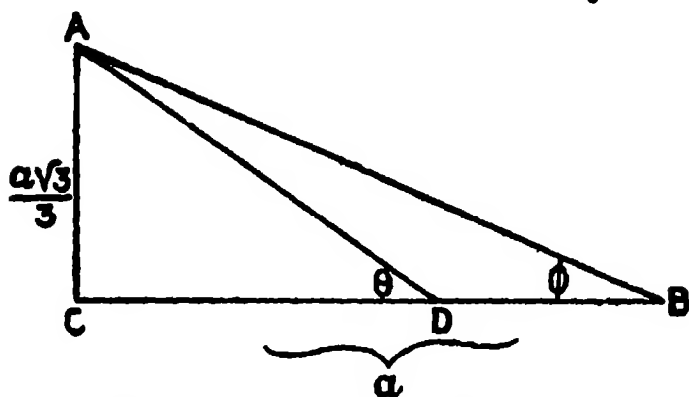
$$\frac{\sin \theta}{a\sqrt{2}} = \frac{\sin (75^\circ + \theta)}{2a}$$

This gives  $\theta = 39^\circ 24'$  approximately

This construction amounts practically, to the construction of a  $\Delta$  of sides  $2a$ ,  $a\sqrt{2}$  and the included angle  $75^\circ$ .

Another construction to a better approximation may be given as follows,

Take a triangle ABC rt  $\angle$  at C with sides  $a$  and  $\frac{a\sqrt{3}}{3}$



$BC = a$  Measure  $CD = \frac{1}{4}$  of  $a$  This means divide  $CB$  into 25 parts and take 17 parts upto  $D$  Then the

angle  $\phi = \tan^{-1} \left( \frac{a\sqrt{3}}{3} / a \right) = 30^\circ$  and the angle  $\theta = \tan^{-1} \left( \frac{a\sqrt{3}}{3} / \frac{17a}{25} \right) = 40^\circ$  approximately

This construction is better as it gives the result correct to within two decimal places. This latter construction is not also inconvenient from a practical standpoint if 25 divisions of a scale are used as the starting length

# NEW LIGHT ABOUT AN ANCIENT INDIAN ASTRONOMER'S FIRST POINT OF THE ECLIPTIC

By

A. E. PALKAR

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(*Synopsis*.—For the last hundred years or more, the Western scholars are of the opinion that the Indian astronomers calculated the places of the planets, the sun and the moon from zeta-Piscium. Amongst the Indian astronomers of the present generation, there is a sharp controversy over this point. In this thesis, it is definitely shown by means of *new circumstantial evidence* that one of the ancient astronomers namely Ganesh Daivadna did not hold ζ Piscium as the first point of the ecliptic. Also it is proved incidentally that alpha-Orionis is the principal star of Ardra.)

Mr. John Bentley, a member of the Asiatic Society published in 1823, a treatise entitled "Historical View of the Hindu Astronomy". In this book he had advocated many of his theories, one of these being that ζ Piscium is the starting point of the ecliptic according to ancient Hindu astronomers. Since his days, there has been a sharp controversy amongst the Indian astronomers about their starting point of the ecliptic.

There is one important difference between the Western and Hindu astronomers about the method of calculating the longitude of a celestial body. The Western astronomers calculate the longitude of a heavenly body from the cutting point of the equator and the ecliptic. But the Hindu astronomers have been in the habit of calculating the longitude of a celestial body from some fixed point. A few centuries after the Christian era, this method of determining the longitude of a body from some fixed point came into vogue in India. The exact date, when this method was first used by the Hindu astronomers is not known. It is supposed that in 444 of the Shaka era (i.e., in 522 A.D.) the cutting point of the ecliptic and the equator (i.e., vernal equinox) and the Hindu astronomers' starting point on the longitude circle coincided. But no definite opinion can be expressed about this date. I have determined the view of Ganesh Daivadna who wrote his famous treatise "Grahalaḥva" in 1520 A. D. This book is so widely used and studied by the Hindu astronomers that the more ancient treatises of the Hindu astronomers such as Aryabhata, Brahmagupta, Lalla & etc. have been superseded on the major portion of the

**Hindu continent** One of the striking features of this book namely *Grahalaghava* as compared with the more ancient books on the same subject is that the places of the planets, the sun and the moon can be calculated without the use of trigonometrical functions. In order to understand the usefulness of *Grahalaghava* to ancient Hindu astronomers one must pay attention to the following two handicaps to which they were subject (i) In those days the Hindus had the tables of the sine of angles differing by  $3\frac{3}{4}$  degrees and (ii) all multiplications and divisions had to be done without the use of the logarithmic tables. The calculating machines of the present generation would have been to them a veritable Aladdin's lamp. Hence it was very tedious and troublesome to them to calculate the places of the planets etc., by means of the methods advocated by the still more ancient Hindu astronomers such as Aryabhata, Brahmagupta etc.

It is definitely known that Keshava Daivadna, the father of Ganesh Daivadna was also a great Hindu astronomer and that his son Ganesh Daivadna had studied astronomy under his father's tutorage and that both the father and the son had taken numerous observations of the stars and planets. After taking into consideration all these facts, we can safely draw the inference that Ganesh Daivadna must have definitely fixed upon the starting point of the ecliptic for his *Grahalaghava*. If it can be ascertained that his starting point was not ♈ *Piscium*, some definite insight about the opinion held by the Hindu astronomers of his period will be available to us.

Now one outstanding feature of the ancient Hindu astronomers is that they did not as a rule, give the observations and the exact date of those observations. If they had given the exact date and the observations taken by them, it would have been very useful to later generations. Though the ancient Hindu astronomers did not give their observations with the dates, they introduced many "Bija sanskars" or corrections into the current methods of their times. But these corrections cannot, as a rule, be used in deciding the debatable point of ♈ *Piscium*. As neither the observations nor the corresponding exact dates are known, it is not possible to guess anything with certainty.

I have come across a certain passage of Ganesha Daivadna occurring in *Muhurta Sindhu* —

ग्रामलस्य लवा समध्यगते दाक्षे द्विदिगिर्मिता  
 ग्राम्येसूर्यभुवोभिमेऽष्टमिहिता ग्राम्ये खशकोन्मिता ।  
 चात्रेभ्यश्चभुवोभिर्वेऽगतिरस्यष्टदश सप्तमे  
 पुष्येऽग्राकभुवोऽहिमेऽद्रिगविसा पिष्येऽद्रिभूबाहवा ॥ १ ॥  
 ग्राम्ये दशहशोऽर्यमोऽनुनि नमःसिद्धा करे कक्षरक्  
 त्वाष्ट्रे भ्यगहशोऽनिलेऽभ्यगहशो द्वीक्षे कुनदाभिन ।

मित्रेऽक्षाग्रगुणाः परे रविगुणा मूलेऽद्विर्वता ऋके  
 पंचाख्यमय उत्तरे किशुगुणा ब्राम्हेऽब्धिबाणामयः ॥ २ ॥  
 श्रीयेऽर्का वसुमे गजाश्विन इहान्वीशोऽनुनीलर्तवोऽ  
 जाघ्री वदशुपांतिमेऽब्धि तुरगाः पौष्णेऽब्धिनंदा इमे ।  
 प्रोक्ताः केशवदैववित्तनुमुवा श्रीमद्रणेणेन वै  
 यद्देशे पलभा युगांगुलमिताऽन्यत्रतिमेऽस्यान्तराः ॥ ३ ॥

*Translation* —“When the nakshatra Aswini comes on the meridian, the rising point of the ecliptic is  $102^{\circ}$ , in the case of the nakshatra Bharani it is  $112^{\circ}$ , that in the case of the nakshatra Kritika it is  $120^{\circ}$ , that of Rohini  $140^{\circ}$ , that of Mrigashirsha  $153^{\circ}$ , that of Ardra  $156^{\circ}$ , that of Punarvasu  $183^{\circ}$ , that of Pushya  $196^{\circ}$ , that of Ashlesha  $197^{\circ}$ , that of Magha  $217^{\circ}$ ; that of Purvafalguni  $232^{\circ}$ , that of Uttaraphalguni  $240^{\circ}$ , that of Hasta  $251^{\circ}$ , that of Chitra  $263^{\circ}$ ; that of Swati  $277^{\circ}$  that of Vishakha  $291^{\circ}$ ; that of Anuradha  $305^{\circ}$ , that of Jeshta  $312^{\circ}$ ; that of Mula  $327^{\circ}$ , that of Purvashadha  $345^{\circ}$ , that of Uttarashadha  $351^{\circ}$ , that of Abhijit  $354^{\circ}$ , that of Shravan  $12^{\circ}$ ; that of Dhanista  $28^{\circ}$ , that of Shatataraka  $61^{\circ}$ , that of Purva Bhadrapada  $66^{\circ}$ , that of Uttara Bhadrapada  $74^{\circ}$ , and of Revati  $94^{\circ}$ ; This is stated by Ganesh the son of Keshava Daivadna, and these figures will be true in the case of a place having four “Palabha” (*i.e.*, having the latitude of  $18^{\circ} 26'$ ), but at other places, there will be small differences” Now the date of this author’s widely known and circulated book of Grahalaghava is 1442 of the Shaka era (*i.e.*, 1520 A. D.) and he must have made the above mentioned observations prior to this period. Now as these are the observations about fixed stars and not about the planets, even a difference of some 20 years would not amount to even  $1/3$  of a degree due to the precession of the equinox. The ascending point of the ecliptic is to be observed on the eastern horizon at a place having four palabha : *e.*, a place having the latitude of  $18^{\circ} 26' 6''$  Nandigram or Nandagaum, the native place of Ganesh Daivadna has the latitude of nearly  $18^{\circ} 26'$ , and so we are certain that he obtained the figures mentioned in the verses by actual observations.

Out of the 28 stars, mentioned in his verses, *only those* can be relied upon which were near the celestial equator. The necessity of this condition can be explained thus a star which has much declination towards the north will appear to stay for a longer period on the meridian “belt” and a star having much southerly declination will appear to move rapidly on the meridian “belt”. Secondly the point of the ecliptic which will be ascending when a particular star is on the meridian should not make a very large angle  $OE^*$ ; otherwise the points on the ecliptic will not be rising with the same speed (*i.e.* angular

\* The angle of the rising point of the ecliptic with the East-West line,



motion per unit of time) as the star on the meridian. By meridian "belt", I mean a small strip of the sky made up by two parallel circles at a very small distance (say  $\frac{1}{2}$  degree) on either side of the meridian. The stars will appear to be on the meridian circle to an observer with rudimentary instruments when they are within the meridian "belt".

Hence these two conditions are absolutely necessary if we have to use the data given by Ganesh Daivadna with confidence.

It is certain that he must have taken his observations either with primitive instruments such as Ghatika (Indian water clock), Nalika-yantra (the Indian astrolabe) etc. or by simple observations. For it is known that the chronometer or the telescope or other modern instruments which can give very accurate results were unknown to Indian astronomers of those days. The Indian astronomers drew their conclusions about the apparent motion of the planets etc. by taking a large number of observations with simple instruments, for a long period.

Now when the criteria—namely the star on the meridian as well as the rising point of the ecliptic should be very near the equator—be applied to the 28 stars quoted in the above mentioned verses, two only can be selected out of the 28 stars and the rest must be refused. These two are Ardra and Shravan.

But about the principal star of Ardra there is some difference of opinion. Mr. John Bently and Raobahadur Chhatre were of the opinion that the principal star of the Indian lunar mansion Ardra is 133 Tauri. But authorities like Colebrooke, Whitney, Burgess, Bapudeo and Ketkar are of the opinion that Alpha Orionis is the star of Ardra, while Dikshit alone held the view that Gamma Geminorum is the principal star. No reliable inference can be drawn unless this difference of opinion be settled with certainty. So I shall examine the opinions of these persons.

Now these different opinions arose because Bentley, Chhatre and Dikshit supposed that  $\alpha$  Orionis is a star comprising the lunar mansion (nakshatra) Mriga (deer). But if we take into consideration that the proper names of that lunar mansion is Mrigasheersha (head of the deer) and not Mriga (deer) alone, then there can be no difficulty in assigning  $\alpha$  Orionis as the star of Ardra. Bentley and Chhatre took 133 Tauri as the principal star of Ardra which is much removed towards the north of Orionis. But Dikshit could not acquiesce himself with 133 Tauri which is of 5.2 magnitude. Hence he chose  $\gamma$  Geminorum which has the magnitude of 1.9.

Again it should be noted that those lunar mansions (nakshatra) which are constituted by a single star cannot have a star like 133 Tauri, the magnitude of which is 5.2, e. g. (i) The nakshatra Chitra is composed of one star namely the Spica and the Spica is of 1.2 magnitude.

(ii) The nakshatra Swati is made up of one star namely the Arcturus & the Arcturus is of 0.2 magnitude. Therefore, the only star of Ardra cannot be 133 Tauri the magnitude of which is 5.2. It may be noted, in addition, that stars of the 5th and 6th magnitude are only visible when the sky is quite clear and also when the bright moon is not in their vicinity. Again it is worth noting that Bentley expressed with great diffidence his view that 133 Tauri is the star of Ardra. For on page 104 of "Historical View of the Hindu Astronomy" he placed the sign of interrogation after 133 Tauri. So when it is known that Bentley himself is not confident about 133 Tauri and that scholars like Colebrooke, Whitney, Burgess, Bapudeo and Ketkar are of the opinion that  $\alpha$  Orionis is the star of Ardra, we can very safely set aside 133 Tauri. The opinion of Dikshit will be scrutinised at the end of this essay and it will be proved there that he was quite wrong in assuming  $\gamma$  Geminorum as the star of Ardra.

It is also worth noting that all the ancient Indian astronomical works such as Nakshatra Kalpa, Vridhagargiya-sanhita, Varaha-mihir, Khanda-Khanyaka, Ratna-kosha of Lalla, Shakalyabrahma-sidhanta, Ratnamala of Shripati, Muhurta-mala, Muhurtachitamani, etc., unanimously say that the lunar mansion of Ardra has only one star. Also the following verse known under the name of Mulanusari-sphuta says that the lunar mansion of Ardra is like mani (jewel)

त्रिमिर्गुणस्य मणिरूपमेक इमं चतुर्मिञ्जितयेन वाणः ।

(Meaning—Mrigashirsha has three stars of the form of the mouth of a deer, Ardra has one star like mani i.e. jewel, Punarvasu has four stars like a house, Pushya has three stars like an arrow.) So  $\alpha$  Orionis which is of 3 to 1.1 magnitude must be the only star of Ardra to sparkle like a jewel and the star 133 Tauri which is of 5.2 magnitude can never possibly be the star of Ardra.

Now let us find out by calculations the rising point of the ecliptic at the time of Ganesh Daivadna when  $\alpha$  Orionis used to come on the meridian at a place, the latitude of which is  $18^{\circ} 26'$ . On the 1st of January 1920, the R. A. of  $\alpha$  Orionis is  $87^{\circ} 42' 49''$  and the declination is North  $7^{\circ} 23' 33''$ . The obliquity of the ecliptic is  $23^{\circ} 26' 54''$ . By changing these co-ordinates, we get:—

$$\begin{aligned}\text{Longitude} &= 88^{\circ} 59' 51'' \text{ \& } \\ \text{Latitude} &= 16^{\circ} 1' 58'' \text{ South.}\end{aligned}$$

Also in 400 years the precession of the equinox—

$$\begin{aligned}&= 50.26'' \times 400 \\ &= 5^{\circ} 35' 4''\end{aligned}$$

Therefore in the days of Ganesh Daivanya, the longitude of  $\alpha$  Orionis is got by deducting  $5^{\circ} 35' 4''$  thus

$$\begin{array}{r} 88^{\circ} \quad 59' \quad 51'' \\ 5^{\circ} \quad 35' \quad 4'' \\ \hline \end{array}$$

$$83^{\circ} \quad 24' \quad 47'' = \text{long. of } \alpha \text{ Orionis.}$$

But the latitude of a star remains the same.

The corresponding R. A. for  $\alpha$  Orionis having the longitude of

$$\begin{array}{r} 83^{\circ} \quad 24' \quad 47'' \quad \text{and the latitude of} \\ 16^{\circ} \quad 1' \quad 58'' \text{ is } 82^{\circ} \quad 18' \quad 3''. \end{array}$$

Now 400 years ago when the star  $\alpha$  Orionis having the R. A. of  $82^{\circ} \quad 18' \quad 3''$  came on the meridian, the point of the ecliptic on the eastern horizon will be  $172^{\circ} \quad 40' \quad 6''$  and the angle OE (i. e. the angle made by this point with the East-west line will be only  $3^{\circ} \quad 2' \quad 8''$ )

Now it may be noted that Ganesh Daivadna did not know the correction for the refraction. Therefore this correction must be added. So

$$\begin{array}{r} 172^{\circ} \quad 40' \\ 0^{\circ} \quad 33' \\ \hline 173^{\circ} \quad 13' \end{array}$$

Therefore  $173^{\circ} \quad 13'$  will be the apparent ascending point of the ecliptic on the eastern horizon.

It must be specially noticed that, I have followed this tedious process of twice changing the co ordinates and then finding out the rising point of the ecliptic instead of using the easy method of the annual variation. For a period of 400 years, the figures for annual variation are not reliable and hence these cannot be used in the present case.

Now it will be seen that the apparent rising point of the ecliptic is  $178\frac{1}{2}$  during the days of Ganesh Daivadna. But in the verses quoted from "Muhurtasundhu," it is said that the rising point of the ecliptic is  $156^{\circ}$  when  $\alpha$  Orionis comes on the meridian. Therefore deducting  $156^{\circ}$  from  $173\frac{1}{2}$  we get  $17\frac{1}{2}^{\circ}$ . This must be *approximately* the distance according to Ganesh Daivadna between the true vernal equinox of those days and the Hindu astronomers' starting point of the ecliptic. But in those days  $\zeta$  Piscium was at a distance of  $13\frac{1}{2}$  from the vernal equinox.

I have already noted that Ganesh Daivadna and Keshava Daivadna his renowned father and preceptor in astronomy had made that science their lifelong study and occupation. It may be noted also that Ganesh Daivadna's views were accepted by his *immediately succeeding generations*. Thus his treatise superseded the works of ancient authors for calculating the places of the planets, the sun and the moon. Hence it is settled that Ganesh Daivadna who had taken actual observations was of the opinion that the Hindu astronomers'

starting point on the ecliptic is some point other than  $\zeta$  Piscium and that this point is at a distance of about  $17^\circ$  from the vernal equinox.

I shall give another *corroborative evidence*.

In the case of the lunar mansion Shrivana, it is unanimously admitted that  $\alpha$  Aquilae is the principal star. The R. A. of  $\alpha$  Aquilae or Altair is  $296^\circ 42' 42''$  on the 1st of January 1920 and the declination is North  $8^\circ 39' 22''$ . The obliquity of the ecliptic is  $23^\circ 26' 54''$ . By changing these co-ordinates, we get  $300^\circ 38' 52''$  as the longitude of  $\alpha$  Aquilae and the latitude of it is  $29^\circ 14' 28''$  North. The precession of the vernal equinox in 400 years is  $5^\circ 35' 4''$ . Therefore the longitude of  $\alpha$  Aquilae must be  $295^\circ 3' 48''$  in the days of Ganesh Daivadna. The latitude remains the same. Now by again changing the co-ordinates we get the R. A. of  $\alpha$  Aquilae to be  $291^\circ 52' 35''$ . This was the R.A. of  $\alpha$  Aquilae in the days of Ganesh Daivadna. When this star came on the meridian at a place having the latitude of  $18^\circ 26'$ , the ascending point of the ecliptic on the eastern horizon was  $27^\circ 27' 18''$  and the angle OE was  $11^\circ 9' 49''$ , and by adding  $33'$ , the correction of refraction, we get  $28^\circ 0'$ . But Ganesh Daivadna says that the rising point of the ecliptic is  $12^\circ$ . Hence the distance of the vernal equinox from the Indian astronomers' starting point on the ecliptic was  $16^\circ 0'$  in the days of Ganesh Daivadna.

In the case of the lunar mansion Ardra, this distance was found to be  $17\frac{1}{4}$  so there is a difference of  $1\frac{1}{4}$  degrees. But this difference can very easily be accounted for. Firstly the angle OE in the case of Shrivana (i.e.,  $\alpha$  Aquilae) is  $11^\circ$  which is rather large and in the case of Ardra (i.e.,  $\alpha$  Orionis) this angle is  $3^\circ$  only. Secondly Ganesh Daivadna had to take his observations with the help of rudimentary instruments. Therefore it is but natural that small discrepancy is very likely to arise in noting the ascending point of the ecliptic which makes such a large angle OE of  $11^\circ$ . However it is not at all necessary to enter into minute details whether  $17\frac{1}{4}$  or 16 is the more correct value. Even with either of the value namely 16 or  $17\frac{1}{4}$ , it proves that Ganesh Daivadna and his contemporaries did not think that  $\zeta$  Piscium was the starting point of the ecliptic.

Finally the case of  $\Upsilon$  Geminorum advocated by Dikshit will be considered

This star may be similarly treated as was done in the case of  $\alpha$  Orionis and  $\alpha$  Aquilae and the rising point of the ecliptic, may be found out when  $\Upsilon$  Geminorum came on the meridian in the days of Ganesh Daivadna. It will be found after the calculations that the rising point of the ecliptic was  $182\frac{1}{2}$ . This value is *inconceivably* wrong with the circumstance of the case. Because if  $\Upsilon$  Geminorum be accepted, then in the days of Ganesh Daivadna, the distance between the Hindu astronomers' starting point and the vernal equinox of those

days amounts to  $26\frac{1}{2}$ . This absurd result cannot be got by rudimentary instruments or by even bare observations of the eye alone!! And hence  $\gamma$  Geminorum cannot possibly be the star of Ardra. Dikshit was led to think that  $\alpha$  Orionis cannot be the star of Ardra, because it is part of Mriga (deer) and hence some other star of first or second magnitude near about  $\alpha$  Orionis should be the star of Ardra. But as already pointed out Mrigaasheersha (head of the deer) and not Mriga (deer) is the proper designation of the lunar mansion preceding Ardra.

*Conclusion :—*

This method which is based upon the actual observations of Ganesh Daivadna, does not require the *exact date* of the observations obtained by him. A difference of even 25 years will produce at the most a change of  $1/3$  degree. Also the observations are free from any prejudice as there was no bitter controversy in his days about the starting point of the ecliptic. He must have adopted the view as was then prevalent throughout the major Hindu continent, with some minor changes of his own. Also these observations are of the nature of *circumstantial evidence*. Hence they are important in giving an insight about the opinion of Ganesh Daivadna and his contemporary astronomers about their starting point of the ecliptic. They held *impliedly* that  $\zeta$  Piscium is not the starting point of the ecliptic and that this point was at distance of about  $16\frac{1}{2} \pm \frac{1}{2}$  degrees from the vernal equinox of their days. The quantity  $\frac{1}{2}$  degrees is introduced from the fact that the correction for refraction was never detected by the ancient astronomers, therefore I have taken  $\frac{1}{2}$  degree as the value of "probable error".

## DIETETICS: FOOD AND RACE

*By*

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We are living in the twentieth century, a century in which science has made a most extraordinary progress in all directions. Of all the investigations made during the last 20 or 30 years those made in the science of dietetics will hold a no mean place, for they have a vital bearing on the improvement of the human race. The conclusions to which Major-General Sir McCarrison and other workers in the same field have come as a result of their investigations on food, have been most far-reaching and have given a new hope to man. He is now no longer helpless as before when he was under the false notion that climate was the principal factor in influencing the health and growth of the body. McCarrison has conclusively proved that it is not so much the climate as food which plays a vital part in producing a strong healthy man or a weakling suffering from all sorts of ailments. Climate one cannot control but food one can and therefore it is that a new world of hope and cheer has opened out before man inasmuch as it is completely within his power to maintain good health and efficiency and improve his race by taking advantage of the latest researches on dietetics.

If science has shown what a powerful weapon the knowledge about food is in the hands of man for making the race healthy, strong, physically fit and efficient what steps should be taken to bring about this result in a country like ours where an epidemic like influenza can sweep off, at one fell swoop, more people in one year than the great war had done in four years, showing how low the vitality of the people and their resisting power against disease must be. An important advance would be made if well-balanced dietaries catering to all tastes and suitable to all purses were prepared. India is a poor country and therefore the dietaries must be very cheap. It is, therefore, very necessary to make investigations to find out cheap but at the same time nutritious substitutes of food materials to replace the costly ones. India is, again, a country so vast and varied in respect of climate, altitude and soil that it is in a position to produce successfully every variety of grain, millet, bean and other food materials. Every effort must, therefore, be made to grow in our country food-stuffs of our own and other countries which have been

found by experiment and experience to satisfy the physical, chemical-bio-chemical, physiological and economical tests e.g., soya bean, (vide page 253)

This naturally brings into prominence the importance of establishing Institutes of Nutritional Research in every Province in a big country like India and directs our attention to the intimate connection they should have between the Agricultural Departments on the one hand and the Industrial Centres on the other. To the former they would suggest problems of research such as that of studying the best conditions under which a food-stuff like Soya bean can be grown in our country and to the latter they would suggest the need of doing propaganda work among the industrial population for a large use of certain food-stuffs which have been found to be best and of making an adequate provision for their supply at a very cheap rate and in an unadulterated form. They would also be helpful in preparing the dietaries mentioned above

It is to the important investigations on food-stuffs carried out by F Gowland Hopkins in England, by Osborne and Mendel, McCollum and Davis in America and by E. Abderhalden in Germany that we owe our present knowledge of the new values of nutrition and the new standpoints in the study of nutrition. It is to the investigations of these men and particularly to the researches carried out by McCarrison in India on the Indian food stuffs and their bearings on health and disease and physical efficiency that I shall refer, now and again, in the course of this article, to show how they vitally affect the question of the improvement of the human race.

Major-General Sir McCarrison, Director of Nutritional Research at the Pasteur Institute, Coonoor, South India, in the evidence he gave before the Royal Labour Commission three years ago made the following memorable statement on the relation of food to the physical efficiency of Indian workers "The level of physical efficiency of Indian workers is, above all else, a matter of food. No other single factor, race, climate etc. has so profound an influence on their capacity to sustain arduous labour and prolonged muscular exertion. Nowhere in the world is this outstanding influence of food more conspicuously illustrated than in India. As we pass from the North-west regions of the Punjab down the Gangetic Plain to the coast of Bengal, there is a gradual fall in the stature, body-weight, stamina and efficiency of the people. In accordance with this decline in many characteristics it is of utmost significance that there is an accompanying gradual fall in nutritive value of the dietaries, and more especially in the average level of protein metabolism attained by the people of the Punjab, United Provinces, Behar and Bengal.' Lt. Col.D.McCay of the Indian Medical Service reached these conclusions

some 20 years ago as a result of his nutritional researches ; my investigations have served to confirm their accuracy. This decline in physical efficiency extends also to inhabitants of the Southern and Western parts of the Indian Peninsula. It depends almost entirely on the gradually diminishing value of the food with respect to .

- A. The amount and quality of its proteins.
- B. The quality of the cereal grains forming the staple article of the diet.
- C. The content and the quality of the fats in food
- D. The vitamin and the mineral content of the food."

The same idea gains further support by the evidence adduced to solve the following questions Is it because of the preponderating race diet that the Japanese, the Chinese, the Javanese and other oriental races are short in stature? Again, is it because the Polynesians, the Northern Europeans, the Sikhs, the Punjabis and the Pathans hit upon a dietary conducive to greater growth that they are taller in stature? Let us examine the evidence on the subject.

It was found by Japanese Scientists that by changing the dietaries of certain school-going children the children who received a diet augmented by food used by the taller races were found to be several inches taller and several pounds weightier than the children who were fed on the normal diet of the country

There is a German proverb which says 'Man ist was er isst' (a man is what he eats). This view was further confirmed by experiments carried out on rats. The rat is an excellent animal for purposes of these experiments. They are both vegetarians and carnivorians and as their metabolic processes resemble those in man the effects of food upon rats are often analogous to those upon men. Again, the young of these animals grow and breed rapidly and medical scientists are therefore able to observe the changes taking place in their organisms within a few days or weeks at the most and consequently to draw accurate conclusions from experiments carried out on them under experimental conditions.

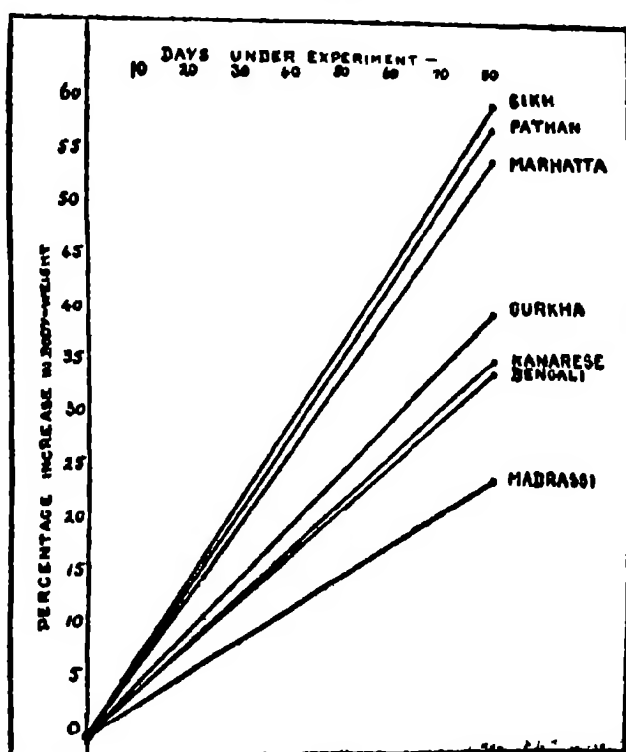
In the discussion of the question on the relationship between climate, food and soil on the one hand and physical efficiency, health, resisting power against disease, capacity for endurance and hard work etc., on the other it was difficult to decide which of the three factors climate, food or soil played the most important part. This question was very ingeniously solved by McCarrison by selecting Coonoor, a beautiful spot on the Nilgiri Hills, 6000 feet above the sea level, reputed for its salubrious climate, as the station for his classical experiments and by the strictly scientific conditions under which he carried them out. He had the following factors constant for all his experiments, viz. climate



and soil, the only factor which he varied was food. McCarrison as a result of the experiments made under the above-mentioned conditions was able to come to some most important and far-reaching conclusions as to the effect of food upon the health, stature, stamina, physical efficiency, etc. of the rats, for food was the only factor which he varied, keeping all other factors constant throughout the experiments. He did not arrive at these conclusions by making one or two experiments but a large number extending over a period of three years over hundreds of rats all of which pointed to the same conclusion.

# RELATIVE VALUES OF THE NATIONAL DIETS OF INDIA.

DIAGRAM 1\*

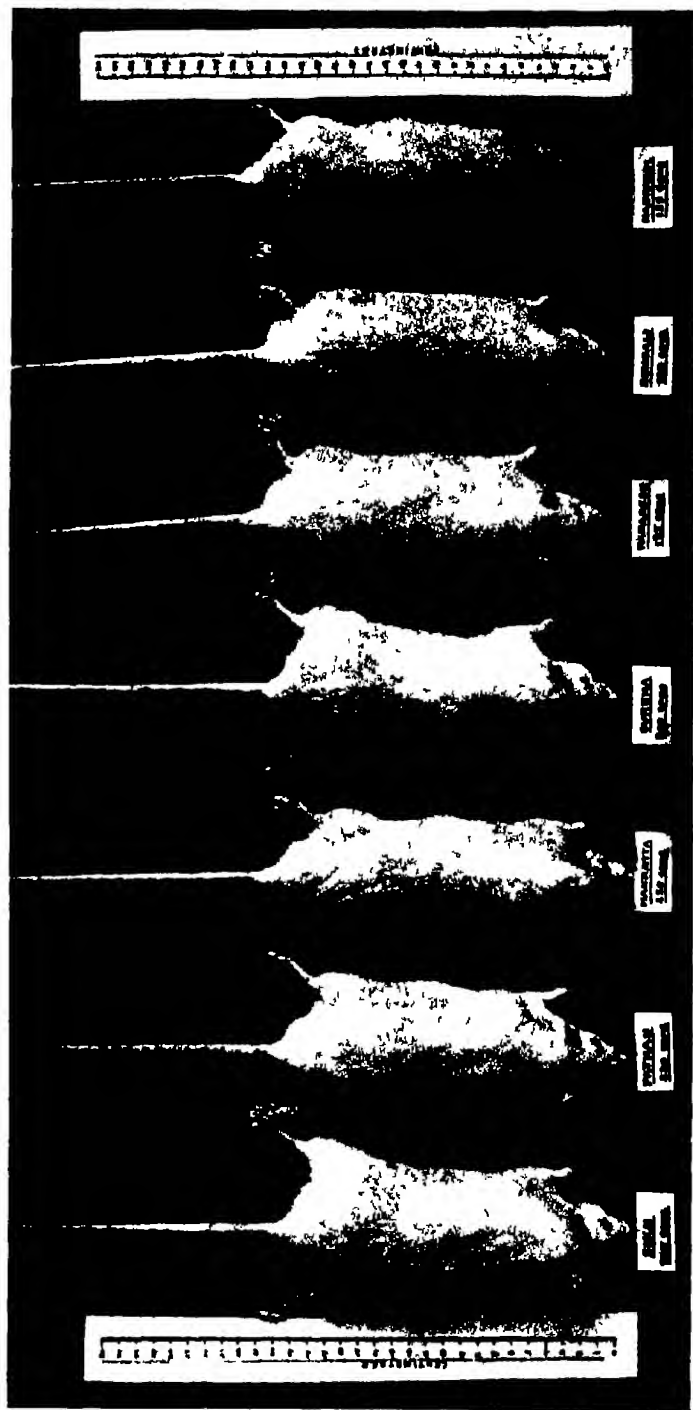


Graph to show growth in the weight of rats during the experiments in feeding on the diets of different races.

In one of the classical experiments devised by McCarrison to find out the nutritional values of the diets of different Indian races he fed rats on the dietaries of the following races, viz. Sikhs, Gurkhas, Marathas, Pathans, Kanarese, Bengalis and Madras and found that

\* By Courtesy of Major-General Sir McCarrison.

AVERAGE SPECIMENS OF COLONIES OF RATS REARED ON THE NATIONAL DIETS OF INDIA  
 DIAGRAM 2\*



SIKH      PATHAN      MAHRATTA      GURKHA      KANARESE      BENGALI      MADRASSI

\* By kind permission of Major General Sir Robert McCarrison



the percentage increase in body weight of rats fed on the Sikh diet after 80 days was the highest (60) while that for the Madrassi diet for the same period was found to be the lowest (18). Diagrams 1 and 2. give a vivid picture of the effect of food on the growth and size of the body. The Sikh and Madrassi diets which were given to the rats in these experiments are shown in Appendix A.

The conclusions regarding the relative physical efficiency of the different Indian races arrived at by McCay and McCarrison have been independently confirmed by Prof. Vaidyanathan from the investigations made by him on the height, weight, chest and abdominal measurements of 51,186 Lives of Hindus from different provinces of India Assured with the 'Oriental Life Office.' He states in his report<sup>1</sup> "There is no questioning the fact that the Punjabi is the best of all Indian types when the comparison is based upon weight given height and age." The second place is given by him to the Hindus of the United and Central Provinces and Bengal. As regards the two remaining groups of Hindus, *viz.* the Madras Hindu and the Bombay Hindu he states "There is no question but that these two classes carry the tail end of the whole Hindu Group."

In the second experiment devised with the same object McCarrison fed rats on the habitual diet of the poorer classes in Europe and compared it with that of the Sikhs. The results of the experiments were that the rats of the Sikh group were of much larger size with smooth coats and gentle demeanour while those of the European group were stunted in growth, had rough coats, a nervous disposition and suffered severely from diseases of various kinds. These experiments show that change in national diets may change national characteristics in the future; they also show the relative nutritional values of the national diets of different races.

In the other experiments devised by McCarrison to find out the relationship between food and health on the one hand and food and disease on the other, he observed the following conditions *viz.*, he used the same animal houses, the same cages, the same scrupulous cleanliness, the same duration of exposure to the sun's rays and under the same salubrious climate of Coonoor. In one series of experiments he took a community of rats and fed them on a well-balanced diet— "a diet similar to that eaten by certain races of Northern India, among whom are to be found some of the finest physical specimens of mankind".<sup>2</sup> What was the result? During the period of experi-

1. Report on an 'Investigation into the Height, Weight, Chest and Abdominal Measurements' of Lives Assured with the 'Oriental Life Office' between the years 1914 to 1924 by L. S. Vaidyanathan, M.A., F.I.A., Deputy Actuary of the 'Oriental Life Office' and Professor of Actuarial Science, the Sydenham College of Commerce and Economics, Bombay.

2. From an article by McCarrison on "Food. The Foundation of Health."

mentation which extended over a period of three years there had been "no case of illness among these rats, no deaths from natural causes in the adult stock, and but for a few accidental deaths, no infantile mortality . . . . Both clinically and at postmortem examinations they have been shown to be remarkably free from disease. Disease and death have been excluded almost completely by minute attention to three environmental conditions *viz.*, cleanliness, comfort and food".<sup>1</sup> In the other series of experiments he took different groups of rats and fed them on different kinds of diets which were ill-balanced, or in other words, were deficient or preponderating in one or more important constituents of food, faulty in one way or another, containing too much of one thing or too little of another. As McCarrison wanted to learn how the foods eaten by the people of India are related to disease he took care to see that the materials of food which formed the various faulty dietaries given to rats under experimentation were usually those ordinarily used by the people of India. These were so combined as to form one sided dietaries disproportionately rich in starches and carbohydrates and lacking in certain elements and complexes necessary for normal nutrition. The results of these experiments were remarkable. Whereas the well-fed rats remained free from disease, the ill-fed rats showed the following morbid states both clinically and at postmortem examinations "Pneumonia and other diseases of the lungs, diseases of the nose and the passages leading from it; diseases of the ear causing pus formation, adenoids, diseases of the eye which may lead to actual blindness, diseases of the stomach and the intestines such as inflammation of the bowels and ulcers, stone in the bladder and kidney and inflammation of the bladder, premature birth of the young or their death in the mother's womb, diseases of the skin such as loss of hair dermatitis and abscesses, anæmia, dropsy, enlarged glands, goitre, neuritis, beri-beri, disease of the heart. And when other animals, such as guinea pigs, are improperly fed scurvy, decaying teeth, rickets or softening of the bones, colitis, dysentery and other diseases occur amongst them".<sup>2</sup> This shows that mankind in general suffers from one major disease—*Malnutrition*—and that many of the maladies from which it suffers arise principally from this cause.

McCarrison found also some other peculiarities in which the ill-fed rats differed from the well-fed ones *viz.*, that the former were often nervous and irritable and if they lived together in colonies, the stronger preyed upon the weaker while the well-fed ones were placid, good-tempered and tractable. These experiments on rats on a large scale and extending over three years as well as experiments made on other species of animals *viz.*, guinea-pigs, rabbits, monkeys and

1 From an article by McCarrison on "Food The Foundation of Health,"

2. *Ibid.*

pigeons undoubtedly showed that keeping all other factors the same and changing only one factor *viz.*, food, the well-fed animals were practically free from disease and ill fed animals suffered from diseases of many kinds. It is reasonable therefore to assume that the human species would be no exception to this rule.

The question which naturally arises out of these considerations is whether it would be possible to keep children practically free from disease as McCarrison was able to do in the case of animals. The answer is in the affirmative. It has been shown by Miss Margaret McMillan of the Nursery Schools, London, that ailments acquired by children as a result of faulty nutrition could be got rid of by proper attention to their diet. She writes in her book (*The Nursery School* 1930), "after the weakly and ill conditioned children have been nurtured and properly fed by her for three or four years they are almost all cured of any ailments from which they may have suffered on their entrance to the school." The most important conclusion which McCarrison has reached from the numerous experiments made by him on different species of animals for a period extending over three years is that faulty feeding is the cause of so many defects one sees in the building of the body and of so many ailments one comes across in children and that disease and physical inefficiency in later life are to be traced to these defects consequent on faulty feeding.

There are many factors affecting the health and physique of the industrial workers, of all these *food* plays the most important part. The Royal Commission on Labour in India 1931 draws attention at many places in its report to the important question of physique and dietary and the part played by defects of dietary. Writing about the cotton mill workers in Bombay it states that 'the low grade of physique among these people is largely due to poor constitutions from birth and to a deficient diet'. Writing about the cotton mill workers in Ahmedabad it states that 'the immigrants from Kathiawar, Rajputana and the United Provinces, who work in Ahmedabad, have a better physique than the local labour force, the variation again being due to differences in diet'. Writing about the Bengal Jute Mill workers it states that 'operatives from up country are usually sturdier than the Bengalis and evidence indicates that the emigrant from North India ordinarily resists industrial fatigue well, his diet and constitution standing him in good stead'. Writing about the miners it states that 'the satisfactory physique of the Santals is attributed to a better dietary and to the fact that they return regularly, often every week-end, to their village homes'. While reviewing the health conditions of the chief groups of Indian industrial workers it states that "impaired physique and defective diet are, however, features common to many and the severe handi-

cape to industrial development which these factors represent demand attention from all concerned."

The following examples taken from McCay's book<sup>1</sup> show clearly the relative productive capacity of the poorly-fed Indian and the better-fed English worker .—

	England	India
Operatives per 1000 spindles	4 2	28
Operatives per 1000 looms	43	125
Annual outturn of yarn per operative	7736 lbs.	4000 lbs.
Weekly outturn of cloth per operative	767 yds	240 yds
Working hours per week	55½	80
Working hours per year	2775	4120

The above figures are pre-war figures. The working hours per week at the present day are 48 for England and 60 for India.

The figures given by Arno S. Pearse<sup>2</sup> when making a comparative statement between (1) a cotton mill in the Southern States of America and a first class cotton mill in Bombay both turning out the same kind of cloth and (2) an up-to-date Bombay mill and an Oldham Mill of the same size, are recent and very illuminating .—

	America	Bombay
(1) No of spindles	23000	25000
No of looms	800	800
Working hours per week	60	60
No. of hands	329	970
Production per man	250 9	81.6
	England	Bombay
(2) Production per man per hour	6.4	3.79

In a statement made by the Ahmedabad Millowners' Association to the Tariff Board in 1926 the following facts were mentioned .

" . . . . . about the close of the last century whereas an operative in Bombay worked on an average only 40 spindles, his contemporary in Italy worked 80 spindles, in Alsace 100, in Switzerland and Bavaria 150 each, or approximately four times as many as an operative in Bombay. The German operative worked during the same period 170 spindles approximately, whereas an operative in England on an average (in 1887) 333 spindles, or over eight times as many as an operative in Bombay (1895). There can be no comparison whatsoever between the spindles managed by a single girl operative in the U. S. A. and those managed by an operative in Bombay. Bombay's

1. "The Protein Factor In Nutrition" by McCay (1911)

2. "The Cotton Industry of India" by Arno S. Pearse (1930)

'40 spindles per operative' would appear as a drop in the ocean before American's 896 to 1200 spindles per operative."

Arno S. Pearce in his Report on the cotton Industry of India 1930 gives the following figures: speaking about Japan he writes, "Operatives work as many machines as can be attended under fair conditions, actually upto three sides of a spinning frame and 5.5 looms per operative (against one side and less than two looms in India)."

Though the wage per operative is much lower in India than in England and Japan yet the cost of production in India is much higher than in Japan and England; this is principally due to the poor efficiency of the Indian operative, this again is due, among other causes, to his frail constitution which results from his unsound feeding, and living under insanitary conditions. In calculating the outturn of cloth or yarn per operative in different centres one has to consider the counts of yarn, the type of machine etc, it is, therefore, difficult to give comparative figures. But as regards the relative productive capacity of the Indian and English and Japanese operatives there are no two opinions that the output per operative in India is less than in England and Japan.

If we now turn our attention to the yearly output of coal per man working in a coal mine which perhaps gives the best comparative tests of the capabilities of two classes of workers (well-fed Europeans and ill-fed Bengalis) we get the following figures:—

England	300 tons.
Germany	243 "
Bengal	80 "

The physical conditions were all in favour of the Bengali and yet the result is an outturn barely 27% of that of the European (McCay).

If we take the average outturn of bricks per day per man in Ahmedabad and compare it with that of the old-fashioned brick-maker of the United States of America we get the following figures:—

	U. S. A.	India
Average outturn of brick a day per man	450	262

Take again the case of a young Bhutia woman of 18 years of age; she is known to carry a load of 200 lbs. over long distances and uphill tracts. To work 12 hours every day is not an unusual thing to a Punjabi Agriculturist.<sup>1</sup> This capacity for endurance and hard work depends largely, according to McCay, on the level of protein metabolism to which their food enables them to attain. The output of work in each case is in direct relation to physical efficiency which again is a result of the constitution of food.

1. Vide Appendix C.



If the physical efficiency of a worker is, above all, a matter of constitution of his food as has been shown above and if the output of work is in direct relation to his physical efficiency it is not a matter of surprise that the output of our ill-fed Indian labourer is very small. If that is actually the case then what steps should be taken to increase his physical efficiency and consequently his output of work. Would the average Indian worker even if he possessed the means to provide himself with a diet which would satisfy his physiological needs actually spend his money on suitable food or know how to choose a well-balanced dietary? Very probably not. McCarrison puts forward a most important suggestion in this connection which deserves the most careful consideration of our industrialists and the directors and owners of our textile mills and other big works. He suggests that 'where possible workers be provided daily as part of their earnings with a properly constituted meal or that they receive part payment in kind in the form of food-materials' The trouble involved in this would be more than repaid in the increased output of work.

This proposal of providing a properly 'constituted meal' to mill operatives is no longer in deliberative or experimental stage in Japan. It is gratifying to note that the mill authorities there supply food to practically all their workers, all food supplies could be had 20 to 30% cheaper at the mill stores than in the town. The description given by Arno S. Pearse in his report on the *Cotton Industry of Japan and China* (1929) about the dining halls attached to the mills is worth noting by our millowners here. "The dining halls are plain, specklessly clean, and the kitchens are like special factories. The food is carefully selected according to the latest Scientific caloric contents and supervised by doctors"<sup>1</sup>

The facts noted above show that stature, body weight, stamina, capacity for endurance and hard work, resisting power against disease, physical efficiency, output of work,—all these depend upon the dietaries of the different classes and races of men. The output of

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1 The proposal of opening big communal kitchens in mill area for the labouring population where only smokeless fuel would be used was made by the author of this paper as one of the remedies to diminish the smoke nuisance in the city due to domestic smoke at the Smoke Abatement Conference held in Ahmedabad under the Chairmanship of the President of the Ahmedabad Municipality in 1931. It was gratifying to him to note that his proposal which was supposed to be impracticable was not only anticipated but actually successfully followed in Japan by the Mill authorities there. It was equally gratifying to him to note that a similar proposal of providing meals to the workers in the mills was made by Major-Gen Sir McCarrison in the evidence he gave before the Royal Labour Commission in the year 1927 but from a different point of view viz., to increase the physical efficiency of the Indian workers.

work by the human machine is closely related to the quality of food with which it is provided. Does this mean that one has to spend more money to get better and more nutritious food? No, it is not so the most essential thing is to know how to prepare a *well-balanced* diet. An ordinary dietary containing simple wholesome foods in the right proportion is far better and cheaper than a dietary consisting of rich foods but which are not properly balanced. To understand this we must know the chemical composition and the biological values of the different food-stuffs that we eat and which are necessary for the physiological needs of the body

Our body is made up of the following elements —

Non-metallic elements Oxygen, Carbon, Hydrogen, Nitrogen, Phosphorus, Sulphur, Chlorine, Fluorine, Silicon

Metallic elements —Calcium, Potassium, Sodium, Magnesium, Iron, Manganese

These elements are combined together in various proportions to form the following groups of substances of which the body is composed

*Water*—present in all tissues

*Salts*—present in all tissues

*Proteins* are complex organic compounds which contain carbon, hydrogen, oxygen and nitrogen and sometimes sulphur, phosphorus and iron

*Fats* are compounds of glycerine with fatty acids.

*Carbohydrates* are substances like starch, sugar or gum and contain carbon, hydrogen and oxygen, the latter two elements in the right proportion to form water, they are therefore called carbohydrates.

For convenience of study the food principles may be further classified as follows

Tissue formers & Body builders

Proteins

Salts

Water

Work and heat producers.

Proteins

Carbohydrates

Fats

The main function of animal life is oxidation. More oxygen is used than the weight of all solid foods. When air is inhaled oxygen which is present in it is abstracted by the hæmoglobin (red colouring matter) of the blood in the capillaries of the lungs. Living in close rooms lowers the vitality to an extent little dreamt of by many.

We need food for two purposes .

(1) to maintain our body heat and

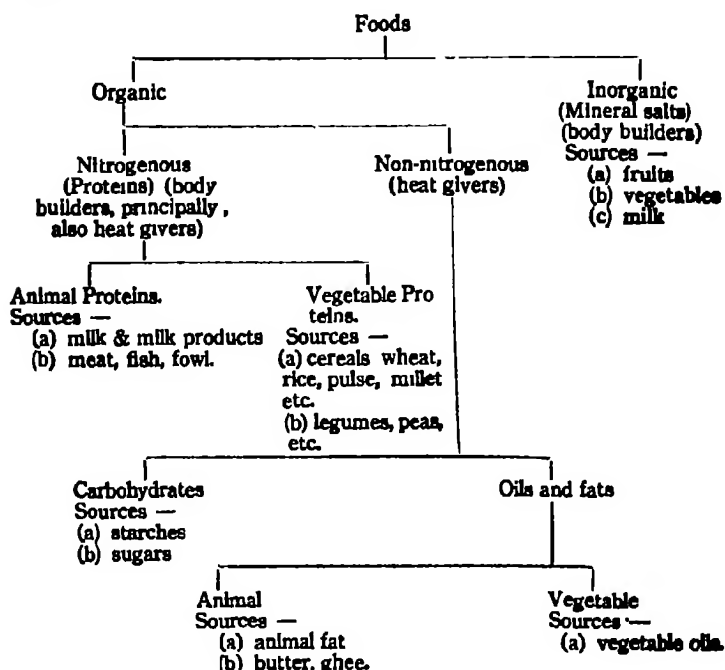
(2) to produce new cells and to make up for the wear and tear of our bodies.

Food-materials are, therefore, divided into two principal classes (1) heat and energy producers and (2) body builders and tissue formers.

Carbohydrates, oils and fats are heat givers,

Proteins, mineral salts and water are body builders.

A complete classification of foods is shown in the diagram given below,—



All foods must be subjected to the following six tests in order to ascertain their relative value —

1 The Physical Test—How much potential energy is the food capable of yielding ?

2 The Chemical Test—What percentage of each nutritive principle (protein, carbohydrate and fat) does the food contain ?

3 The Physiological Test—How does the food behave in the stomach and intestine ?

4. The Biological Test—What vitamins and how much of each does the food contain ?

5 The Economic Test—Are the nutritive constituents of the food obtained at a reasonable cost ?

And shall we add also

6. The Psychological Test—Is the food palatable ?

Let us now examine these tests somewhat in detail.



DIAGRAM 3



This Food Star illustrates beautifully the proportions of the different constituents of food which will make a well balanced diet. It also brings into prominence the important part played by air, water and sunlight as constituents of Food. This Food Star should serve as a Pole Star throughout life in matters of food.

(By kind permission of Major General Sir Robert McCarrison and Messrs. Macmillan & Co., Ltd., Madras.)

**The Physical Test.**—The food-stuffs that we eat differ in their power to produce energy; their 'energy-value' varies; it can be measured in 'calories'. A calorie is the amount of heat required to raise the temperature of one kilogramme (2·2 pounds) of water through one degree centigrade. One gramme of pure protein and carbohydrate has each an energy value of 4 calories. One gramme of fat has an energy value of 9 calories. According to McCarrison an Indian in prime of life requires each day from 2,500 to 3,500 calories according to the part of India in which he lives and the nature of work he has to do; an Indian woman requires four-fifths of this amount, or from 2,100 to 2,900 calories.

**The Chemical Test.**—The following proportions of proteins, fats and carbohydrates in their diets are recommended for Indians living in different parts of India —

	North of India	South, South-east and South west of India
Proteins	90 to 100 grms	60 to 70 grms.
Fats	80 to 90 „	50 to 60 „
Carbohydrates	360 to 450 „	Sufficient to make the total
Total calories	2,520 to 3,010	requirement of calories

Again the proportion of animal protein should not be less than 33% of the total protein in the diet and that of animal fat not less than 50% of the total fats in our diet. Only when our dietary contains food stuffs which yield proteins, fats and carbohydrates in the proportions given above will it be said to be well balanced and to properly fulfil its function (Diagram 3). It is not enough to know that the protein, fat and carbohydrate are in the right proportion but it should also be seen that they are of the right kind. An animal fed on gelatine (protein), olive oil (fat), and straw (carbohydrate), no matter how much of each is given, would not keep healthy and would eventually meet with certain death for the food constituents are not of the right kind.

What is wanted is the right weight of the body according to the height and age of the individual, neither underweight nor overweight, that is an indication of good health. "Mens sana in corpore sano". Body and mind are so intimately related and act and react so much on each other that a sound mind naturally results from a sound body.

The principal defects of Indian diet are (1) too little suitable proteins, (2) too little animal fat and (3) a large excess of carbohydrates. The best way to make up for deficiencies in the first two is to use plenty of milk and milk products and green leafy vegetables and fruits. Two examples of well balanced and two of badly-balanced diets, are given in the Appendix C which bring out the facts mentioned above very clearly, also an example of an average diet used in one of the local students' hostels (Appendix D.)

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*The Physical Test*—The food-stuffs that we eat differ in their power to produce energy; their 'energy value' varies; it can be measured in 'calories'. A calorie is the amount of heat required to raise the temperature of one kilogramme (22 pounds) of water through one degree centigrade. One gramme of pure protein and carbohydrate has each an energy value of 4 calories. One gramme of fat has an energy value of 9 calories. According to McCarrison an Indian in prime of life requires each day from 2,500 to 3,500 calories according to the part of India in which he lives and the nature of work he has to do, an Indian woman requires four fifths of this amount, or from 2,100 to 2,900 calories.

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The proportions of proteins, fats and carbohydrates in some of the important Indian food-stuffs with their vitamin contents and the amount of calories they yield are given in Appendix B. One can easily find out from this table whether one's diet is well- or ill-balanced.

*The Physiological Test.*—The food to be digestible must be capable of being absorbed but it should also contain some residue of husks or fibres which would act as a ballast in the intestine. If a food is cent percent digestible it would produce constipation. A thorough mastication of the food is also essential. Again it should be stated that it is not what a man eats that gives him strength but what he digests and assimilates.

*The Biological Test* —Over and above the proteins, fats, carbohydrates, mineral salts and water we require certain other substances in our food which are body builders and are essential to life, they are called vitamins, their absence or deficiency in food prevents growth of body, gives rise to certain diseases, known as deficiency diseases and ultimately produce death. They are present in such infinitesimally small quantities in the foods that only some of them have yet been seen or weighed.<sup>1</sup> They are like a spark which ignites the fire of nutrition. They are all present in the foods which nature supplies us for our use but we should see that we do not inadvertently spoil our foods by removing the vitamins from them or by killing the vitamins in them before we eat them

The law of growth of animal life is that it must depend for its subsistence upon plant life. Men and animals have not got a mechanism in their physical bodies to make their own food as the plants do. They must have it prepared for them by the plants, directly or indirectly, for the plants are organisms endowed with a capacity for transmuting inorganic minerals into organic ones and for manufacturing the most vital food-factors, the vitamins. It is now well known how important these organic minerals and vitamins are not only for maintaining the bodies but also for building them.

The classical experiments carried out by Gowland Hopkins on two groups of rats conclusively prove the important part played by the vitamin A in the growth of animals. The open circles in diagram 4 indicate rats fed on artificial milk (absence of vitamins), solid black dots indicate rats fed on artificial milk plus a teaspoonful of natural milk containing the vitamin A. It will be seen from the diagram that the rats fed on artificial milk diet only were losing in weight and the other group which was given a teaspoonful of natural milk along with the artificial milk was gaining in weight, this went on till the 18th day when the experiment was reversed and the diets were exchanged with the result that those which were losing weight now began to grow and

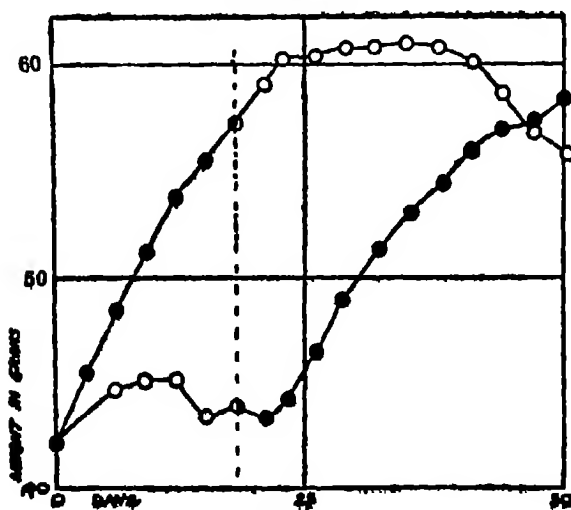
1. Vide Appendix I.

gain in weight and those which were increasing in weight now began to lose weight and grow languid. Again a diet deficient in vitamin A causes also inflammation of the eye, lungs, intestines, bladder etc; the first of which may even end in total blindness in some cases. A dog suffering from ophthalmia as the result of a diet deficient in vitamin A was cured in 10 days by the addition to his diet of 20 cc. of cod-liver oil per day (Stenlock, Nelson and Hart). An adequate supply of this vitamin causes not only growth but is one of Nature's surest safeguards against infection from pathogenic bacteria. Vitamin A is slowly destroyed by cooking

Experiments made on pigeons fed on polished rice and unpolished rice showed a similar result. The polished rice are wanting in an important vitamin B which is present in the unpolished rice. Those fed on polished rice began to lose their appetite, became very thin, suffered from diarrhoea, got paralysis and died, but if to the polished rice were added the rice polishings in time then the tragedy was averted. A dog suffering from marked paralysis of hind legs as the result of a diet lacking in vitamin B was cured in a short time by supplying that vitamin in the form of tomato juice (Cowgill and Mendel).

Experiments by Gowland Hopkins on two groups of eight rats.  
Solid black dots—artificial milk + 3 cc. fresh natural milk  
(a small teaspoonful)  
Open circles—artificial milk only. (Basal diet)

**DIAGRAM 4.**



### Growth curves showing the influence of Vitamin A on rats.

It was noticed that sailors used to suffer from a disease called scurvy during long voyages when they could not get fresh vegetables and fruits to eat. In this disease the gums become sore and bleed, the legs swell and pain, this is prevented or those suffering from this disease recover if they are given the juice of lemons. This is because green leaves, vegetables and fruits contain another vitamin called C. This vitamin is killed by cooking, storing and tinning.

Rickets, a disease of darkness and civilisation, is another malady known to be associated with food which is wanting in vitamin D, which is usually present in milk, butter, eggs or cod-liver oil. A child living in a dark and gloomy house, who does not get enough milk or who is fed on milk from a cow that has been kept in a dark stable contracts this disease. But if the child lives in open sunlight, or the milk and cow are exposed to sufficient sunlight, or subjected to ultra-violet rays then the disease does not occur. The story of the discovery of the Vitamin D is most fascinating. It has brought out most clearly the correlation between darkness and disease. The natural method of procuring Vitamin D is to eat foods containing ergosterol which is fortunately very widely distributed in all kinds of natural food-stuffs and then to have this activated in the skin by the ultra-violet rays of the sun. The understanding of the mechanism of the formation of Vitamin D has brought into prominence the health giving properties of sun-light and the important part played by the skin, —a vital organ of the body as a reservoir of light to human welfare. Anything which prevents the direct access of sunlight to skin such as a cloudy atmosphere, smoke pollution of the air, clothes, indoor life, means so much loss to health and physical efficiency. The rationale of light clothing and open-air life will thus be evident.

It is impossible to write all about this interesting and important subject in a short article like this. I would strongly recommend those interested in this subject and who are anxious to prepare their dietaries on right lines to read the excellent little booklet by Major-Gon. Sir McCarrison on Food which could be had for the trifling price of As. 12/- only but which is worth its weight in gold.

*The Economic Test* —A lunch of bread and skim milk at 2 annas yields as many calories (i. e. heat and energy) as a lunch of soup, beef, potatoes, turnips, bread, butter, milk and sugar in coffee at 8 annas; it is therefore more economical as it is 4 times cheaper.

Of all the foods milk is the ideal food and of all the milks mother's milk is the best for an infant. The health of an infant depends so much on its mother's milk and the quality of the milk depends so much on the food the mother takes that too much attention cannot be given to her diet which should be properly balanced. Suppose the diet of the mother is deficient in calcium, phosphates and vitamins

which are essential for the formation of teeth and bones, her milk will also be deficient in these salts and vitamins; now if the infant is fed on such a milk there is no wonder that it will suffer from rickets or that its teeth will be bad; with such a handicap from the very beginning it will have less resisting power against disease, and will, therefore, practically be a weakling incapable of carrying on the ordinary duties of life. How far reaching the results of a well- or ill-balanced diet are is evident from the above example. Again an infant is likely to suffer from anemia if fed exclusively on milk diet for more than six months for milk is deficient in iron and deficiency in iron leads to impoverishment of the blood and check in growth.

The best form in which milk should be taken in our country is in the form of sour milk, curds etc. when one is not absolutely sure of the purity of the fresh milk. Whole wheat and unpolished rice are always to be preferred to white flour and polished rice. Tea and coffee have no food values (vide appendix B).

Of the combinations bread and milk and bread and apple, milk was found to be superior to apple as a nutritional supplement of bread, for of two rats (twin sisters) of equal size and equally healthy and vigorous at weaning time the one fed on bread and milk grew to five times the initial weight while the other fed on bread and apple remained stationary (Sherman, Rouse, Allen and Woods 1921).

Of the combinations bread and milk, bread and butter and bread and meat the first was found to be superior to the other two from the point of view of growth.

Attention is drawn here to the importance of the use of the Soya bean as a very nutritious article of food in our country where the bulk of people do not use animal food. In one ounce of the Soya bean we get 9.6 grms. of proteins, 4.9 grms of fat and 9.5 grms of carbohydrates. It also contains three vitamins A, B, and D and its proteins have a relatively high "biological value." In fact from the study of the properties of the Soya bean it is expected to be a cheap and valuable substitute for meat, milk, egg and cod-liver oil. Soya bean crop is extensively grown in China and is used in various ways in human nutrition in China and Japan. It is very necessary that such an article of food should be produced<sup>1</sup> on a very large scale in our country and supplied very cheap to the people and its use popularised.<sup>2</sup>

The facts given above show what an important subject the subject of nutrition is; how vitally it is connected with questions of health and disease, of physical and industrial efficiency and output of work, and

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1. It is gratifying to note that experiments carried out in Sindh, Poona etc. show that the Soya bean can be successfully grown in our country.

2. For further information regarding the composition and uses of the Soya bean vide Appendices E, F, G and H.

with the all important question of producing various types of the human race. *"As knowledge with regard to the effects of food upon man increases, it is more than conceivable that races that first avail themselves of the new values of nutrition may decrease the handicaps of disease, lengthen their lives and so become the leaders of the future".* (Food and Race, by Victor Heiser, Foreign Affairs, Vol. VI. Page 427.)

If India is to become a strong and virile nation then it is the duty of Government, Municipalities, Educational and other public bodies and the leaders and panchayats of every community to see that no boy or girl leaves the school without getting an adequate knowledge of the important subject of dietetics and that no section of the public is without cheap and scientific dietaries suitable to its taste, purse and need.

In the preparation of this article I have drawn upon freely from books and journals treating of food and vitamins. To the authors of all these papers I desire to express my thanks. To Major-General Sir McCarrison and Principal G. Findly Shirras my special thanks are due for placing at my disposal a good many materials on the subject. I am again grateful to Major-Gen. Sir McCarrison and Messrs. Macmillan and Co., Madras, for permitting me to reprint diagrams 1, 2 and 3.

## APPENDIX A. \*

### SIKH DIET.

(As given to the rats—Diagrams 1 and 2.)

Whole wheat chapatis.  
Green vegetables in plenty.  
Butter.  
Sprouted gram.  
Fresh milk in plenty.  
Occasionally meat.

### MADRASSI DIET.

(As given to the rats—Diagrams 1 and 2.)

Rice.  
A small quantity of dhal and vegetables.  
A small quantity of ghee.  
Tamarind water.  
Little buttermilk.  
Betel nuts.

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\* This shows the Sikh and Madrasai diets on which the rats were fed by McCarrison in the classical experiment described on page 241.

APPENDIX B.\*

Proteins, fats and carbohydrates in grammes per ounce, calorie-value and vitamin content of common food materials used in India :—

Food-stuffs.	Proteins in Grms.	Fats in Grms.	Carbohydrates in Grms.	Calories per Ounce.	Vitamins.			
					A	B	C	D
<i>Milk and Milk-Products</i>								
Cows' Milk	0.94	1.02	1.36	18	† † †	† †	†	†
Human Milk	0.42	1.50	0.75	18	† to ††	†	...	.. †
Cream	0.70	5.24	1.27	55	† † †	†	...	†
Cheese	7.35	8.88	0.50	111	† †	V.L.	...	..
Butter Milk	0.85	0.14	1.36	10	†	†	†	.
Skimmed Milk	0.96	0.08	1.44	10	†	†	†	.
Dadhi	1.40	1.00	0.80	18	† †	†	†	.
Sheep's Milk	1.50	2.00	1.41	30	† † †	†	†	†
Goat's Milk	1.21	1.13	1.21	20	† † †	†	†	†
Buffalo's Milk	1.35	2.18	1.24	30	†††	†	†	†
<i>Flesh, Meat and Eggs</i>								
Lean Beef	6.20	2.06	..	43	V.L.	†	V.L.	†
Lean Mutton	5.97	1.98	..	42	V.L.	†	V.L.	†
Goat's Meat	7.20	0.75	..	36	0	†	V.L.	0
Pork	6.05	3.14	..	53	0	†	0	...
Bacon	5.00	15.00	..	155	0	..	..	..
Liver	6.11	1.70	0.76	43	† † †	† † †	†	†
Kidney	4.54	1.36	0.06	31	† †	† †	..	..
Brain	2.90	2.77	..	37	†	† †	..	..
Tongue	4.41	5.43	..	67	0	†	..	...
Fat Fish	5.32	3.70	...	55	† † †	†	..	...
Non fat Fish	5.15	0.20	...	22	†	†	..	...
Freshwater Fish	5.50	1.15	..	32	†	†	...	..
Chicken	6.74	0.38	..	30	†	..	...	..
Duck	5.80	2.94	...	50	†	†	...	..
Pigeon	6.25	1.86	...	42	†	†	..	...
Egg	3.79	2.97	...	42	††	† † †	...	†
<i>Animal Fats</i>								
Beef fat, Mutton fat	0.34	26.40	..	239	† †	...	...	...
Lard	..	26.80	..	241	to V.L.	...	..	...
Butter and Ghee	..	23.10	...	208	† † †	..	..	...
Cod-liver Oil	..	28.00	..	252	† † †	V.L.	...	† † †
Fish-liver Oil	...	28.00	...	252	† † †	V.L.	..	† †
<i>Vegetable Oils</i>								
Cocconut Oil	..	28.00	..	252	†	0	0	V.L.
Gingelly Oil	..	28.00	..	252	V.L.	0	0	0
Linseed Oil	..	28.00	..	252	V.L.	0	0	...
Ground-nut Oil	...	28.00	..	252	V.L.	0	0	V.L.
Olive Oil	..	28.00	..	252	V.L.	0	0	...
Cotton-seed Oil	..	28.00	..	252	V.L.	0	9	...
Mustard Oil	...	28.00	...	252	0	0	0	...
Cocogen	...	28.00	...	252	0	0	9	...
Margarine	..	23.80	...	214	0 to †	0	0	...

\* Reprinted from 'Food' by Major-Gen Sir McCarrison by kind permission of the author.



Food-stuffs.	Proteins in Grms.	Fats in Grms.	Carbohydrates in Grms.	Calories per Ounce	Vitamins.			
					A	B	C	D
<i>Sugars and Starches</i>								
White Sugar	..	..	28.30	113	0	0	0	...
Brown Sugar	..	..	26.89	108	0	0	0	...
Goor or Jaggery	0.08	..	25.00	100	0	V.L.	0	...
Honey	0.11	..	20.21	81	V.L.	V.L.	0	...
Tapioca	0.05	0.01	24.83	100	0	0	0	..
Sago	2.18	0.04	22.00	97	0	0	0	...
Sugar Cane	0.42	0.16	6.20	28		†	†	...
<i>Cereal Grains &amp; Bread</i>								
Wheat (atta)	3.90	0.54	20.35	102	†	††	0	...
White Flour	3.14	0.37	21.54	102	0	V.L.	0	...
Unpolished Rice	2.30	0.085	22.30	99	V.L.	†	0	...
Washed Rice	1.62	0.15	26.34	113	0	0	0	..
Polished Rice	1.79	0.13	26.09	113	0	V.L.	0	...
Parboiled Rice	1.84	0.22	26.11	114	0	†	0	...
Ragi or Bajri	2.78	0.46	23.35	109	† to ††	††	0	...
Cambu	3.64	1.38	19.40	105	†	††	0	...
Cholam	2.90	1.17	19.70	101	†	††	0	...
Barley	2.97	0.62	20.60	100	†	††	0	...
Oat-meal	3.37	2.43	19.81	115	†	††	0	..
Maize (yellow)	2.13	0.48	20.80	96	††	††	0	...
White Bread	2.00	0.33	14.80	70	0	†	0	...
Suji or Semolina	4.00	0.68	14.20	80	†	†††	0	..
Rice Polishing	.				†	††	0	..
<i>Dhals, Peas &amp; Beans</i>								
Fresh broad beans	2.66	0.11	6.45	37	†	††	††	..
Fresh French beans	0.54	0.03	1.38	8	†	††	††	...
Peas (dried)	1.85	0.17	4.75	28	†	††	0	..
Dhals	6.50	0.99	16.20	100	†	††	0	...
Grams	5.70	1.30	16.30	96	†	††	0	...
Soya Bean	9.60	4.70	9.50	119	†	††	0	..
<i>Nuts and Seeds</i>								
Almonds	5.26	15.96	4.30	182	V.L.	††	0	...
Cocconut	1.61	14.31	7.90	167	†	††	0	...
Groundnut	7.30	10.92	6.90	155	V.L.	††	0	..
Walnut	3.85	19.92	3.96	211	V.L.	†††	0	...
Other Nuts	5.00	16.50	3.60	183	V.L.	††	0	...
Linseed	6.40	9.50	7.60	142	† to ††	††	0	...
<i>Tuber and Root Vegetables</i>								
Potato	0.70	0.04	8.15	36	V.L.	†	† to ††	...
Beetroot	0.34	0.03	1.75	9	V.L.		†	...
Celery	0.17	0.03	1.07	5	..	†††	††	...
Onions	0.37	0.03	3.06	14	V.L.	††	†	...
Garlic	1.92	0.03	7.90	40	†	†	††	...
Carrots	0.25	0.03	2.26	10	† to ††	††	† to ††	...
Leeks	0.71	0.03	2.63	14	†	†	††	...
Paranips	0.48	0.14	5.97	27	V.L.	†	† to ††	...
Radishes	0.28	0.03	0.96	5	V.L.	†	†	...
Turnips	0.34	0.03	1.25	7	V.L.	††	†	...
Yams	0.51	0.06	6.31	28	...	†	†	...
Fleshy roots (Taro)	0.50	0.06	6.30	28	..	†	†	...

Food-stuffs.	Proteins in Grms.	Fats in Grms.	Carbohydrates in Grms.	Calories in per ounce.	Vitamins.			
					A	B	C	D
<i>Green Leafy Vegetables</i>								
Brussels Sprouts	0.92	0.06	1.61	11	†	†	††	..
Cabbage	0.39	0.03	1.27	7	†††	†††	†††	..
Lettuce	0.31	0.06	0.54	4	††	††	††	...
Spinach	0.51	0.06	0.82	6	†††	†††	†††	...
Turnip Tops	1.19	0.17	1.78	13	†††	†††	††	...
<i>Other Vegetables</i>								
Tomatoes	0.20	0.03	1.27	6	††	†††	†††	...
Rhubarb	0.17	0.02	1.03	5	..	..	†	...
Cucumber	0.17	0.02	0.57	3	...	†	††	...
Pumpkins	0.28	0.03	1.47	7	...	†	†	..
Brinjal	0.34	0.09	1.44	8	..	†	†	...
Cauliflower	0.54	0.06	1.67	9	†	†	†	...
Bhendi (Ladies fingers)	0.57	0.33	1.70	12	..	†	†	...
Knol-khol	0.26	0.16	3.30	16	V.L.	†	†	...
Artichoke	0.78	0.06	5.00	24	..	†	†	..
Asparagus	0.68	1.00	0.66	14	†	†††	†	...
Potal	0.21	..	0.37	2	...	†	†	...
<i>Fresh Fruits and Berries</i>								
Apples	0.09	0.06	3.54	15	..	†	†	...
Bananas or Plantains	0.45	0.03	2.28	11	V.L.	†	..	...
Grapes	0.17	0.03	3.93	17	..	†	V.L.	..
Lemons	0.14	0.14	0.88	5	...	†	†††	...
Oranges	0.25	0.03	2.69	12	†	†	†††	..
Pears	0.09	0.03	2.29	10	..	†	†	..
Pomegranates	0.18	...	0.19	2	..	†	†	...
Peaches	0.19	0.03	2.66	12	...	..	††	...
Pineapple	0.11	0.09	2.75	12	..	..	††	...
Watermelons	0.11	0.06	1.90	9	..	..	†	...
Papaya	0.16	...	1.10	1	†	†	††	...
Liches	0.84	0.07	1.90	12	..	†	††	...
Mango	0.04	0.22	5.20	23	†	..	††	...
Guavas	0.37	0.20	2.27	12	..	†	†	..
<i>Dried Fruits</i>								
Apricots	1.56	0.09	14.04	63	..	0	0	...
Currants	0.48	0.09	11.89	50	..	0	0	...
Dates	0.45	0.03	19.73	81	..	†	0	...
Figs	0.56	0.14	15.99	67	..	†	0	..
Prunes	0.85	0.09	11.43	50	..	†	0	...
Raisins	0.62	0.09	17.32	73	...	†	0	...
Tamarind	0.39	..	8.89	37	..	†	†	...
<i>Miscellaneous</i>								
Jams	0.06	...	19.81	79	0	0	0	...
Marmalade	0.06	..	19.41	78	0	0	0	...
Treacle	0.06	..	16.95	68	0	0	0	...
Condensed Milk	2.49	2.35	15.31	92	†	†	0	...
Pickles	0.31	0.11	1.13	7	...	...	...	...
Pepper	4.39	2.41	17.83	111	...	..	...	...
Infant foods (Tinned)	3.59	0.93	21.56	109	..	...	0	...
Sandesh	5.40	8.00	12.00	124	0	0	0	...
Tea	...	...	...	...	0	0	0	...
Coffee	...	...	...	...	0	0	0	...

Three Crosses († † †) mean 'rich in',  
 Two Crosses († †) mean 'moderately rich in',  
 One Cross (†) means 'some' or 'poor in',  
 0 means 'none',  
 V.L. means 'very little'.

A blank space in the columns under 'vitamins' means that the vitamin-content has not been estimated,

Calories are given in round numbers,

One ounce equals 28.3 grammes.

## APPENDIX C

### *Examples of well-balanced diets*

#### 1. Punjabi Agriculturist. \*

	Quantity in ozs.	In grammes.		
		Proteins.	Fats.	Carbohy- drates.
Atta (Whole wheat flour)	20	78.00	10.80	407.00
Dhal . . .	1	6.50	0.99	16.20
Vegetables ...	10	3.10	0.60	5.40
Sugar . . .	2	0.16	...	50.00
Curds . . .	4	5.60	4.00	3.20
Butter . . .	2½	..	57.70	..
Milk . . .	20	18.80	20.40	27.20
Buttermilk ... ..	40	34.00	5.60	54.40
Total ...	...	146.16	100.09	563.40
Animal origin ...	..	58.40	87.70	..
Less 10% for waste ...	..	14.61	10.00	56.34
Balance ...	...	131.55	90.09	506.06
Calories ...	...	539.4	837.8	2074.8
Total Calories ...	...	round numbers		3452

\* From the report of the evidence before the Royal Labour Commission by Major-General Sir McCarrison.

## 2. Certain races of Northern India.\*

	Quantity in Ozs.	In grammes.			
		Proteins.	Fats.	Carbo- hydrates.	Calories.
Atta ...	12	46.80	6.48	244.2	1222
Rice (home pounded)	6	13.10	0.51	133.8	595
Meat (mutton) ..	2	11.94	3.96	0.0	84
Milk	20	18.80	20.40	27.2	360
Vegetable oil ...	1	0.00	28.00	0.0	252
Ghee ...	1.5	0.00	34.60	0.0	312
Root vegetables ...	8	4.40	0.36	31.8	148
Cabbage ...	8	3.10	0.24	10.2	56
Mango .	4	0.16	0.88	20.8	92
Dhal ...	1	6.50	0.99	16.2	100
	63.5	105.50	94.42	484.2	3221
Less 10% for waste	6.3	10.50	9.64	48.4	322
Total ...	57.2	95.00	86.78	435.8	2899

## APPENDIX C. (continued).

*Examples of badly balanced diets\**

## 1. The poor Hindu family diet.

	Quantity in Ozs.	In grammes.			
		Proteins.	Fats.	Carbo- hydrates	Calories.
Polished rice ...	21.0	37.60	2.70	547.9	2373
Dhal ...	0.7	4.50	0.70	11.3	70
Black gram ...	0.7	4.00	0.90	10.7	67
Vegetable oil ..	0.1	0.00	2.80	0.0	25
Vegetables ...	2.0	1.10	0.10	7.7	36
Meat or fish ...	0.06	0.40	0.05	0.0	2
Coconut ...	0.05	0.08	0.72	0.4	10
	24.61	47.68	7.97	578.0	2583
Less 10% for waste	2.40	4.76	0.79	57.8	258
	22.21	42.92	7.18	520.2	2325

\* From "Food" by McCarrison.

This diet contains too little protein, all of which is of vegetable origin, far too little fat, too much carbohydrate and not enough calories. It is dangerously low in all the vitamins, especially A and B and it is deficient in salts notably of calcium, phosphorus and iron. The family living on this diet were of low vitality, incapable of sustained hard work and prone to bowel complaints.

## 2. The well-to-do Hindu family diet. (South India).\*

	In grammes.				
	Quantity in Ozs.	Proteins	Fats.	Carbo-hy- drates.	Calories.
Polished rice ..	23.0	41.2	3.0	600.0	2599
Dhal ...	1.2	7.8	1.2	19.4	120
Grain ...	1.9	10.8	2.5	29.0	182
Vegetable oils ...	1.2	0.0	33.6	0.0	302
Ghee ...	0.4	0.0	9.2	0.0	83
Curds ...	9.0	12.6	9.0	7.2	162
Vegetables ...	6.0	2.0	0.5	8.6	48
Cocoanut ...	2.0	3.2	28.6	15.8	334
Sugar ...	1.0	0.0	0.0	25.0	100
Milk ...	7.0	6.5	7.1	9.5	126
	52.7	84.1	94.7	714.5	4056
Less 10% for waste	5.2	8.4	9.4	71.4	405
	47.5	75.7	85.3	643.1	3651

This diet is too poor in animal protein and animal fat, too rich in carbohydrates and too high in calories. It should be adjusted by reducing the amount of rice eaten, by substituting unpolished for polished rice and by increasing the amount of milk, milk-products, green leafy vegetables and fruits.

\* From "Food" by McCarrison.

## APPENDIX D.

Example of an average Diet used at the Kadwa Patidar Vidyarthi-Bhuvan, Ahmedabad.

Food Stuff.	Quantity in Ozs.	Proteins in grams.	Fats in grams.	Carbohy- drates in grams.	Calories.
Wheat ...	7.26	28.33	3.92	147.84	741.03
Rice ...	5.09	11.52	0.42	111.74	495.99
Pulse ...	3.51	22.81	3.47	56.86	351.00
Ghee ...	1.14	0.00	26.33	0.00	237.12
Treacle ...	0.60	0.04	0.00	15.20	60.80
Oil ...	0.80	0.00	22.45	0.00	202.10
Milk ...	8.23	11.11	17.94	10.20	246.90
Vegetables ...	5.85	4.09	0.23	47.67	210.60
Sour Milk ..	0.20	1.70	0.20	0.27	2.04
<b>Total ...</b>	<b>32.68</b>	<b>79.60</b>	<b>74.96</b>	<b>389.78</b>	<b>2547.58</b>
Animal origin ...		13.00	44.27		
Less 10% for waste		7.96	7.49	38.97	254.75
<b>Balance ...</b>		<b>71.64</b>	<b>67.47</b>	<b>350.81</b>	<b>2292.83</b>

This diet contains 26% less in total proteins, 50% less in animal proteins, 21% less in total fats, 12% less in carbohydrates and 16% less in calories. (Vide p 249).

To make it a well-balanced diet more of milk and milk products and green leafy vegetables should be taken.

(The figures given above were kindly supplied to me by my students Messrs. B. H. Patel and P. B. Patel to whom my sincere thanks are due.)

## APPENDIX E.

Re : *Soya bean*.\*

The composition of 'Soya flour' and 'Soya milk' as compared with rice and wheat and milk is as follows

	Soya Flour	Soya Milk	Milk	Wheat	Rice
Protein%	42.0	5.76	3.50	12.2	8.0
Fat%	20.0	2.46	3.50	1.7	2.0
Carbo- hydrates%	24.0	1.40	5.25	73.7	77.0
Water%	9.0	...	...	10.6	12.0
Calories	2.165	...	...	1750	1720
Ash	...	0.84	0.75	...	...

The ash of soya bean contains 6.12 per cent. of calcium and 28.66 per cent. of phosphoric acid.

\* From a letter by Major-General Sir McCarrison.

## APPENDIX F.

*Uses of the Soya-Bean.\**

For very many centuries the cultivation of soya beans, both in China and Japan, has been of the greatest importance to those countries, where they are put to a variety of uses :—

(a) As a foodstuff they are made into —

1. Bean sauce or soy, called in Japan "shoyu" (whence the name "soya") and in China, *chiang-yu*. It is made by boiling the beans adding an equal quantity of wheat or barley, and leaving the mass to ferment, a layer of salt and three times as much water as beans are afterwards put in, when the liquid is pressed and strained.
2. The Chinese paste *chiang*—not the same article of diet as the Japanese paste *miso*. It is made by farmers and eaten with fish, meat and vegetables, while the more expensive Chinese soy is only made by the well-to-do and restaurant keepers, and is not consumed by the poor.
3. *Tou-fu*, or *beancurd*, made from green or yellow beans, the former giving a better yield by being poorer in quality.

(b) The beans are also consumed as a table vegetable and in soups, and in Japan are used in confectionery.

(c) The oil is used as a substitute for lard in cooking. But even in these places, the centres of its origin, neither the soya bean itself nor the meal derived from it, has been used altogether as a staple article of food; it is the spices prepared from the soya bean which have found so extensive a use in these countries, and more especially in Japan, where they are eaten almost with every meal.

The flavour of the soya spice is obtained by injecting mildew fungus into the par-boiled beans, and leaving them in a moist condition at a temperature of from 20° to 25° centigrade, letting them ferment for months, even for years, before being used. It is then only that the savoury soya flavour is fully attained and made to render service as a popular article of food never found wanting in a Japanese household. Furthermore, many fermented products of the soya beans prepared in various ways, have long been consumed in the two countries such as "*miso*", the estimated average consumption of which in Japan alone may be stated at 40 grammes per head daily, "*tofu*", "*natto*" (two different kinds of cheese), as well as the soya milk and soya sauce. Of the latter Japan annually produces 700,000,000 litres of which every Japanese consumes on an average  $\frac{1}{10}$  litre daily.

\* This note was kindly prepared by Major-General Sir McCarrison who had advocated as early as 1927 in his evidence before the Royal Labour Commission the use of the Soya bean.

All these products are obtained by fermentation, thus improving their digestibility—which is not always characteristic of legumes—yielding an important supply of protein so necessary for human diet. The soya bean is one of the few seeds containing the three vitamins A, B, and D which are indispensable in a staple food consumed by mankind and necessary also in food for cattle

The fat contents vary according to the various methods employed in extracting the oil, and are said to average 6 per cent.

## APPENDIX G.

### *Uses of the Soya Bean\**

It has been shown (J H Prentice, R. G. Baskett and G. S. Robertson) that the Soya bean plus mineral mixture bring about the beneficial effect on growth, maturity, egg production and mortality of chicks almost to the same extent as milk.

The Soya bean is rich in valuable nutritive ingredients *viz.*, proteins and fat Starch is practically absent. It is also rich in mineral matter especially in soluble phosphates and potash.

It contains the ferment diastase in considerable quantities. It also contains uralytic ferment which is an important factor in physiological chemistry

The biological value of the Soya bean protein is very high. It contains almost all the important amino-acids, particularly Glycine and tryptophane and lycine. In fact the protein of the Soya bean is very similar to that of cow's milk and animal muscles.

The Soya bean contains lecithin more than any other plant and therefore could be used for cure of nervous diseases. The lecithin of the Soya bean is, according to Dr. J. Freud, identical with that in egg yolk. The Soya bean contains three vitamins A. B. and D.

. . . . .

The Soya bean crop is extensively grown in China and is used in various ways in human nutrition. The young pods are used as green vegetables, seeds are used as vegetables. Sometimes they are allowed to sprout and sprouted grains make an excellent vegetable of high nutritive value. Their milk supply comes from Soya bean seeds which are soaked overnight in water and the juice of soaked seed is then pressed out. That is their milk, which tastes as cow's milk, is used for drinking in tea, for curds, butter milk, cheese etc.

In the course of human nutrition, especially amongst vegetarian India, the Soya bean is expected to play a very important part, if intro-

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\* Extract from a letter from the Live-stock Expert to Government, Bombay Presidency, Poona.



diced. It can be used in the same way as other pulses, e. g., as green vegetable (green seeds), dal, Bhajis, Sev, Papads and various other preparations. It can be allowed to sprout. Sprouted grains can make excellent vegetable. I can say that the Soya bean can be singled out as the best pulse so far known.

The best variety from the feeding point of view is one which contains the greatest fat percentage *vis.*, large yellow mammoth.

#### APPENDIX H.

It is gratifying to the author of this paper to note that a lecture given by him on "Dietetics Food and Race" at Baroda on 7th October 1933, at which a State Officer in charge of Food Stuffs presided and in which the lecturer emphasised the high nutritive value of Soya bean as a food stuff, recommended its extensive use among the people and urged upon the State authorities the importance of growing it in their State, has led to the introduction of the Soya Bean cultivation in the Baroda territories. His Highness the Gaekwar of Baroda performed the ceremony of planting the Soya bean in January 1934.

That a Soya bean Restaurant was run in the H O H. Fete in Bombay where a number of preparations made from Soya bean were served augurs well for the future of this important food stuff.

#### APPENDIX I.

The progress made during the last few years in elucidating the composition and constitution of the three vitamins-A, C and-D and the mastering of the technique employed in their commercial preparation is most remarkable.

The isolation of one full pound of pure crystalline ascorbic acid by Szent-Györgi from Hungarian capicum (cayenne pepper), its identification with vitamin-C, the elucidation of its constitution by the Haworth school and its synthesis by Haworth and Hirst (4th August 1933) read like a fairy tale.

Vitamin D is now commercially manufactured and costs one-eighth its price in cod liver oil. This vitamin is most powerful in its activity—one part in two thousand millions exerts a recognisable effect on rat.

Unlike vitamins-C and-D, vitamin-A has not yet been prepared quite pure and in crystalline form.

The table\* given below gives the composition of the three vitamins-A, C and-D, their chemical nature, their daily human requirements, their physiological activity and the nature of their effect.

Compound.	Daily human requirement.	Dilution which gives detectable physiological effects.	Nature of effect.
Vitamin-A ( $C_{30}H_{50}O$ )	0.875 mgm.	1 in $64 \times 10^4$	Growth "anti-infective. Maintenance of normal structure and function of mucous membranes.
and Carotene ( $C_{40}H_{56}O$ )	1.400 mgm.	1 in $32 \times 10^4$	
Vitamin-C (Ascorbic acid) ( $C_6H_8O_6$ )	40 mgm. to 80 mgm	1 in $1.4 \times 10^4$	"Anti-scorbutic". Maintenance of normal structure and function of blood capillaries.
Vitamin-D (Calciferol) ( $C_{28}H_{44}O$ )	0.25 mgm	1 in $2240 \times 10^4$	Growth "anti-rachitic" or "calcifying" vitamin. Maintenance of normal structure of bones and teeth.

\* "Biochemistry and the Manufacture of Fine Chemicals" by F. H. Carr. [J. S. C. I. (9-2-34) page 113.]

# IMPORTANCE OF DIALYSIS IN THE STUDY OF COLLOIDS.

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Dialysis has been utilised since the time of Graham for freeing a colloidal solution from the impurities necessarily introduced into it at the time of its preparation, *viz.*, the peptising agent and the other electrolytes formed as a result of double decomposition. The importance of the influence of dialysis on the various properties of colloidal solutions has, however, not been generally realised by colloid chemists. In what follows (1) a summary of the results obtained in our laboratory on the variation of the different properties of some colloidal solutions on dialysing them to different extents is presented and (2) the views expressed in previous papers are considered from the point of view of changes in charge as observed by measuring the cataphoretic speed of colloidal solutions under varying conditions.

## (a) *Kinetics of coagulation.*

2. According to Smoluchowski the rate of coagulation of a colloid in the sensitive range of electrolyte concentration is a simple reaction and the equation for rapid coagulation has the form

$$\theta = \frac{1}{Kv_0} = \frac{1}{4\pi Drv_0}$$

where  $\theta$  is the specific coagulation time,  $K$  the velocity constant,  $v_0$  the number of particles at the beginning,  $r$  the radius of the sphere of attraction round each discharged particle and  $D$  the diffusion coefficient. He has distinguished slow coagulation from the rapid by the fact that in the former case all the encounters between the micellae are not effective, but only a proportion which depends upon electrolyte concentration. Thus the expression for slow coagulation according to him will be

$$\theta_1 = \frac{1}{K_1v_0} = \frac{1}{8\pi Drv_0x}$$

where  $x$  is the fraction by which  $K$ , the velocity constant for rapid coagulation, must be multiplied. If this theory is correct, one should be able to pass from a coagulation velocity curve of rapid coagulation to one of slow coagulation at a lower electrolyte concentration by multiplying the time  $t$  by a certain numerical factor, i. e., the curves of

coagulation velocity must be related to one another. Several workers have found that the view of v. Smoluchowski is correct (for references see Desai, Trans. Faraday Soc., 24, 181, 1928; Patel and Desai, *ibid.*, 26, 128, 1930; Desai, Kolloidchem. Beih., 26, 357, 1928).

3. It has however been shown by other investigators (for references see papers of Desai quoted in Para. 2) that the rate of coagulation of a colloid over the sensitive range of electrolyte concentration is not a simple reaction as postulated by v. Smoluchowski and that the rate of slow coagulation has an auto-catalytic character and the reaction velocity can be represented by an equation of the form

$$\frac{dx}{dt} = K(1+bx)(1-x)$$

where  $K$  and  $b$  are constants and  $x$  the amount of change in time  $t$ .

4. The widespread opinion, first put forward by Hardy (Proc. Roy. Soc., 66, 110, 1900) that coagulation begins only when colloidal particles are completely discharged and the iso-electric point is reached, has been found to be erroneous by Powis (Zeit. f. physik. Chemie, 89, 186, 1915). According to him coagulation begins as soon as the electro-kinetic potential or the electric charge falls below a certain absolute value. This value of the electro-kinetic potential, at which coagulation first begins, has been termed by Freundlich the "first critical potential" and is said to have the same characteristic value for any particular sol when coagulated with salts having coagulating ions of different valencies. The experiments of Burton (Phil. Mag., 17, 583, 1909), Kruyt Roodvoets and van der Willigen (Fourth Colloid Symposium, 1926, pp. 304-310) and Kruyt and van der Willigen (Z. physikal. Chem., 130, 170, 1927) have shown that their results also support Powis' theory of critical potential.

5. Freundlich (Colloid and Capillary Chemistry Eng. Translation—1926, pp. 431-447) has utilised the existence of the first critical potential to explain the phenomenon of slow coagulation. According to him slow coagulation begins when the first critical potential value is reached. The slow coagulation passes into rapid coagulation when the value of the potential difference becomes zero or the iso-electric point is reached (Freundlich's second critical potential). In the region of slow coagulation as the particles are still charged, only those collisions are successful in bringing about coalescence in which the velocity of the particles exceeds a certain value. After the iso-electric point is reached all the collisions will be successful although the velocity with which the particles move might be very small in some cases, because there will be no repulsive forces between the particles.

6. Recently Mukherjee and co-workers (J. Indian Chem. Soc., 4, 493, 1927; 5, 697, 1928; Nature, 122, 960, 1928; Special Number of the Journal of the Indian Chemical Soc., 1933, p. 201) have expressed

doubts about the existence of critical potential characteristic of coagulation of a colloid by electrolytes. It should be stated that their conclusion is based on results most of which have been taken with mixtures of electrolytes and non-electrolytes as well as with electrolytes containing organic anions and much credence cannot be given to their conclusions. The charge on colloidal particles of a sol can be varied by changing the amount of the peptising agent in the sol. In our laboratory we have prepared colloidal solutions of ferric hydroxide and thorium hydroxide having different initial charge on the particles by dialysing the sols to different extents and studied coagulation in the presence of  $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{MgCl}_2$  and  $\text{MgSO}_4$ . Details of these measurements will be published in due course (B. N. Desai and S. K. Borkar on Ferric Hydroxide and B. N. Desai and A. K. Desai on Thorium Hydroxide). In the case of colloidal ferric hydroxide, the sol begins to coagulate in all the cases when the cataphoretic speed of colloidal particles is reduced to 25–29 although the two samples of the sol tried had different initial cataphoretic speeds—38 and 54. Similarly the two samples of thorium hydroxide sol having initial cataphoretic speed of 33 and 25 begin to coagulate when the cataphoretic speed of the particles is reduced to 19–21 in the former and 16–17 in the latter case. Differences in the value of the critical charge in individual cases can be easily understood if the preferential adsorption (the word preferential indicating that the ion is adsorbed in the inner sheet of the double layer) of similarly charged ions is considered as suggested by Desai (J. Bombay University, 1, Part II, 25, 1932). The idea of critical potential is thus completely supported by our measurements.

It should be pointed out here that generally it is observed that the value of the cataphoretic speed at which coagulation begins is somewhat higher in those cases where there is a marked preferential adsorption of the similarly charged ions. Why this is so is not quite clear. Some experiments are being undertaken for getting a clear idea of this point.

7 In our papers referred to in para. 2 it has been shown that in the case of colloidal thorium hydroxide the appearance of the S-shaped coagulation velocity (C. V.) curves or demonstration of the auto-catalytic nature of the coagulation process depends on

(i) the suitability of the method employed in following the course of coagulation,

(ii) the concentration of the coagulator,

(iii) the purity of the sol (this can be changed by dialysing the sol), and

(iv) the concentration of the disperse phase. The causes which might be responsible for the non-observance of auto-catalysis due to

factor (i) (suitability of method) have been discussed in detail in our papers.

(ii) Concentration of the coagulator.—As stated in para. 5 slow coagulation begins when the charge is lowered to the critical value (first critical potential) and the slow coagulation passes into rapid coagulation when the iso-electric point (second critical potential) is reached. In the case of concentrated electrolytes the time required to pass from the first critical potential to the second will be very small (in seconds) and therefore with the limitations of the present methods of following the course of coagulation, it will be very difficult to get the S-shape of the C. V. curves. This however will not be the case with dilute electrolytes where the potential difference decreases slowly and the region of slow coagulation extends over some minutes (cf. Powrie, *loc. cit.*), and hence the appearance of the S-shaped C. V. curves. It should however be stated that the C. V. curves are not found to be S-shaped even with dilute electrolytes having multivalent coagulating ions. We have observed that the amount of bivalent coagulating ion required to lower the charge to the critical value is much less than that of univalent coagulating ion. This is due to greater preferential adsorption of the former ions. As a result even with dilute electrolytes containing multivalent coagulating ions if the potential of the double layer is lowered at all, the rate of its lowering will be great in the beginning and hence the rate of coalescence also will be large. At very great dilutions, the coagulation will not proceed far as there is not sufficient electrolyte left to lower the potential difference any further. The coagulation will therefore be partial in these cases. In fact cataphoretic experiments showed that in such cases a greater amount of uncoagulated sol was still left in the mixture. In those cases where there is complete coagulation *i. e.*, with somewhat concentrated electrolytes having multivalent coagulating ions, the time required to pass from the critical value to the iso-electric point will be very small (in seconds) and therefore it will be impossible to observe the slow coagulation phenomenon as in the case of concentrated electrolytes having univalent coagulating ions.

(iii) Purity of the sol.—In explaining the effect of this factor it was assumed by us (Patel and Desai, *loc. cit.*) as done by other workers that the charge on the colloidal particles in the case of thorium hydroxide also decreases continuously with the progress of dialysis. It was argued that as the initial slow coagulation refers only to the process which takes place between the region of the first and second critical potentials, if by any means the time required to pass from the first to the second critical potential is made appreciably small or negligible, the initial and less steep portion of the C. V. curves will also disappear. Continuous lowering of charge with the progress of dialy-

als will help to achieve this purpose and hence for very pure sols the C.V. curves will not be S-shaped. Even with a dilute electrolyte concentration in the case of very pure sols, the C. V. curves will not be S-shaped because the value of the charge being very near the iso-electric point, the time required for coagulation will be very small. Actual measurements of charge in the case of this sol have however shown that with the progress of dialysis the cataphoretic speed first increases, reaches a maximum value and then decreases continuously (Desai, *Current Science*, 1, 38, 1932; 1, 125, 1932; also paper by B. N. Desai and A. K. Desai, *loc. cit.*). The above line of argument therefore cannot be applied to the period of dialysis when the cataphoretic speed continuously increases with the progress of dialysis, as the charge on the colloidal particles will be removed further and further away from the first or the second critical charge. The C. V. curves were found to be S-shaped in the case of sols dialysed for about eight days while for sols dialysed for longer periods (about 14 days) no S-shaped C. V. curves could be obtained (Patel and Desai, *loc. cit.*). As found in the later investigation (B. N. Desai and A. K. Desai, *loc. cit.*) the cataphoretic speed increases with the progress of dialysis up to a period of only about 5 days (the rate of dialysis being almost the same in the two cases) and therefore the cataphoretic speed being regularly decreasing with progress of dialysis after eight days, the previous arguments used for explaining the non-observance of S-shaped C. V. curves for sols dialysed for long periods (very pure sols) still hold good.

(iv) Concentration of the disperse phase.—It was observed by us (Patel and Desai, *loc. cit.*) that when thorium hydroxide sol is coagulated by an electrolyte of the same concentration throughout, the tendency of the C V curves to be S-shaped becomes less and less with an increase in the dilution of the sol. This was explained by assuming that in the case of a dilute sol a particular amount of electrolyte will bring down the charge on the particles more nearly to the critical point or the iso-electric point than in the case of a concentrated sol. This will mean that the time required to reach the iso-electric point after adding the electrolyte to the sol will be less with a dilute sol than with a concentrated sol. With the progress of dialysis as the charge on the particles is brought nearer and nearer to the iso-electric point, the time required for coagulation will be so small with the dilute sol when compared with the concentrated one—the same amount of electrolyte having been added in both the cases—that the C. V. curves may not be S-shaped at all. This effect will be more marked in the case of a sol dialysed for longer periods than one dialysed for shorter periods. Now as stated before the charge on colloidal particles of thorium hydroxide increases in the initial stages of dialysis and therefore the ideas modified under

factor (iii) in the preceding sub-para. should only be applied. Also our later measurements (B. N. Desai and A. K. Desai, loc. cit.) have shown that for samples of this sol dialysed for periods shorter than what corresponds to the maximum in the cataphoretic speed dialysis curve, on diluting the sol, the cataphoretic speed first increases, reaches a maximum value and then decreases, on the other hand, for sols dialysed for longer periods, on diluting the sol, the cataphoretic speed continuously decreases. In view of the evidence of the charge measurements, the previous explanations do not hold good only for those cases in which the cataphoretic speed increases upto a certain dilution. There is however one additional factor which has not been hitherto considered in explaining this influence, namely, the effect of concentration of the disperse phase on the size of the particles. Desai (in paper referred to in para. 2) has shown that the auto-catalytic nature of the coagulation process and the S-shaped C. V. curves may not be observed at all with dilute sols. These can best be observed in fairly concentrated sols which contain a considerably larger number of particles because sufficiently large multiple particles can be formed in them. It is considered that this factor will have a considerable effect on the nature of the C. V. curves.

8. In a recent paper S. S. Joshi and V. L. Narayan (Special Number of the Journal of the Indian Chemical Soc., 1933, p. 41) have studied in detail the influence of wall area in the coagulation of colloidal solutions of  $MnO_2$ ,  $Sb_2S_3$  and positively charged  $Fe_3O_4$ . They have observed that the rate of coagulation is markedly increased in all cases when the wall area of the coagulating system is increased by introducing glass beads. They also find that when the same number of beads and the containing walls are paraffined the coagulation is sensibly retarded in all cases. In the light of their results they consider unlikely that the increase in the rate of coagulation, under wall effect alone, can convert a 'slow' into a 'rapid' coagulation. They conclude that auto-catalysis cannot be considered as a general characteristic of coagulation as has been supposed by some workers, but that it is a secondary process which adds to the main course of coagulation under certain conditions.

Now as shown by electrosmotic, cataphoretic and stream-potentials measurements, the wall-layer of glass in contact with water becomes negatively charged. The nature of this charge will be modified considerably in the presence of electrolytes as well as when the glass surface is paraffined. It is therefore certain that the glass surface will help or retard the coagulation according to the nature of charge on it and on the colloidal particles. Moreover glass walls themselves, whether paraffined or not and whether charged or uncharged, will act as centres for coalescence. In view of these considerations it is not

justifiable to say that the results of Joshi and Narayan (*loc. cit.*) support the conclusion that the nature of coagulation process is not intrinsically auto-catalytic.

On the other hand, their results can well be utilised to show that the nature of coagulation process is auto-catalytic. For as shown by them the walls of the containing vessel (unparaffined) make the S-shape of the C. V. curves less marked and it is quite likely that the non-observance of auto-catalysis by some workers might be to a certain extent due to this effect.

9. In the light of the foregoing evidence it can be stated that as yet no investigator has succeeded in showing that the nature of the coagulation process is not intrinsically auto-catalytic. Failure to observe the S-shape of the C. V. curves and the auto-catalytic nature of the coagulation process can be due to several factors which have been considered in this section and which as shown will considerably modify the nature of the C. V. curves and of coagulation. Also as shown in this section the idea of critical potential is completely supported; if any deviations occur they can be explained by taking the influence of the similarly charged ions into consideration.

(b) *Applicability of Schulze-Hardy law.*

10. It has been shown by Desai (*Kolloidchem. Beihefte*, 26, 384, 1928) that in the case of colloidal thorium hydroxide containing appreciable amounts of HCl, the C. V. curves for equivalent concentrations of different electrolytes having the same coagulating ion (univalent) are not identical and that the C. V. is not the same in different cases. This is in contradiction to the requirements of the Schulze-Hardy law according to which the time required for the coagulation of a sol by electrolytes having the same oppositely charged ion is independent of the nature of that ion of the coagulator which carries the same charge as the colloidal particles. It has been expressed by several investigators (references are given in the above paper of Desai on p 394) that unless and until the influence of the similarly charged ion is taken into consideration, no theory will be adequate enough to explain the results of coagulation of sols by electrolytes. In the case of multivalent coagulating ions the influence of the similarly charged ion being negligible, the Schulze-Hardy law is obeyed. It has also been shown by Desai (*loc. cit.*) that the applicability of the Schulze-Hardy law increases with the progress of dialysis. This has been explained by assuming that with the progress of dialysis the preferential adsorption of the similarly charged ions decreases.

11. The measurements of cataphoretic speed of colloidal solutions of ferric hydroxide (Desai and Borkar, *loc. cit.*) and of thorium hydroxide (B. N. Desai, and A. K. Desai, *loc. cit.*) in the presence



of varying amounts of electrolytes have shown that preferential adsorption of similarly charged ions takes place in the presence of small amounts of electrolytes containing monovalent coagulating ion, while with bivalent coagulating ion no preferential adsorption of similarly charged ions is allowed to take place. It has also been observed that the amounts of different electrolytes necessary to lower the value of the charge to the critical value are not the same. The earlier conclusions are thus supported by the evidence of charge measurements in these respects. The charge measurements, however, show that the preferential adsorption of similarly charged ions does not appreciably decrease with the progress of dialysis *i. e.*, with an increase in the purity of the sol. Therefore the explanation advanced in the previous paragraph about applicability of the Schulze-Hardy law with the progress of dialysis requires modification. In the case of thorium hydroxide the deviations from the Schulze-Hardy law only disappear after a period of dialysis of 10 days or so. During this period of dialysis the charge on the colloidal particles will be brought nearer and nearer to the iso-electric point (the maximum cataphoretic speed having occurred at a period of dialysis of 5 days or so) and thus as shown in section (a), coagulation tends to be rapid in all the cases (disappearance of S-shaped nature of the C. V. curves). Under the circumstances it is quite likely that although different similarly charged ions may be preferentially adsorbed to different extents in the beginning, this may not affect the nature of the C. V. curves to any appreciable extent.

12. In view of the evidence of charge measurements it is also considered that the mechanism of coagulation as pictured by Weiser (J. Phys. Chem., 28, 232, 1924, 29, 955, 1925) and Dhar (*ibid.*, 28, 457, 1924) for explaining the preferential adsorption of similarly charged ions is difficult to understand. For, the preferential adsorption of the similarly charged ions is noticed only in the presence of small amounts of electrolytes and at these concentrations the colloidal solutions do not show at all any tendency for coagulation.

(c) *Relation between charge and stability.*

13. Numerous papers have been published by investigators in Colloid Chemistry on the stability of various colloidal solutions in the presence of electrolytes—greater flocculation value (F. V.) greater stability and smaller F. V. smaller stability. These investigations have been made with colloidal solutions which have been purified to certain extent by dialysis. The decrease in the F. V. with the progress of dialysis has been explained generally by assuming that with the progress of dialysis, the charge on the colloidal particles continuously decreases. We have measured cataphoretic speed and stability simultaneously of colloidal solutions of gold, ferric hydroxide and thorium

hydroxide with the progress of dialysis. The following results have been obtained (for details refer to papers by Desai, Nabar and Barve, *J. Indian Chem. Soc.*, 9, 463, 1932, Desai and Borkar, loc. cit. B. N. Desai, loc. cit.)—

(i) In the case of colloidal gold, with the progress of dialysis both cataphoretic speed and stability as determined by F. V. increase in the beginning, reach a maximum value and begin to decrease simultaneously thereafter.

(ii) The cataphoretic speed of colloidal particles of ferric and thorium hydroxide, first increases, reaches a maximum value and then decreases on subjecting the sols to dialysis; the F. V., on the other hand, continuously decreases with the progress of dialysis in both the cases.

14. The above results show that although there is a direct relation between charge and stability in the case of colloidal gold, the same is not found to be the case with colloidal ferric and thorium hydroxide. In the latter case such relation is only found to exist for the period of dialysis when both cataphoretic speed and F. V. decrease regularly. The reasons for a regular decrease in the F. V. with the progress of dialysis, in spite of first an increase and then a decrease in the cataphoretic speed, have also been advanced by us. In both the cases—ferric as well as thorium hydroxide—an increase in the preferential adsorption of the stabilising ions in the presence of KCl (electrolyte added for F. V. determinations) as well as a change in the size of the particles during dialysis have been found to be very significant from the point of view of stability. In the case of ferric hydroxide the changes in the hydration of colloidal particles in the initial stage of dialysis are also partly responsible for the abnormal behaviour.

15. It has been observed by us that on adding small increasing amounts of KOH in the case of gold sol, of HCl and  $\text{FeCl}_3$  in the case of ferric hydroxide sol and of HCl in the case of thorium hydroxide sol, the cataphoretic speed first increases and then decreases or that there is a maximum in the cataphoretic speed (C. S.)—concentration (C) curve. The initial increase in the cataphoretic speed is due to a preferential adsorption of the similarly charged ions. All these sols initially contain an amount of the stabilising electrolyte which is appreciably more than what corresponds to the maximum in the C.S.—C curve for that electrolyte. With the progress of dialysis, the amount of the stabilising agent continuously decreases. The process of dialysis can therefore be considered as a reverse of the process of adding small increasing amounts of the peptising electrolyte to the colloid in so far as the removal of the peptising electrolyte is concerned; one should thus expect that with the progress of dialysis the cataphoretic speed will first increase and then decrease. Thus a col-

loidal solution when subjected to dialysis will show (a) first an increase and then a decrease or (b) a continuous decrease of the cataphoretic speed according as it initially contains an amount of the peptising agent (a) more than or (b) equal to or less than what corresponds to the maximum in the C.S.—C curve with that electrolyte. Other sols are being investigated from this point of view.

16 From the foregoing it will appear that it is not safe to draw conclusions about changes in charge from the stability determinations as has hitherto been the practice, for although this may serve a useful criterion in some cases it may not do so in others

*(d) Changes in cataphoretic speed and stability of colloidal solutions of ferric and thorium hydroxide dialysed and diluted to different extents*

17. We have observed (Desai and Borkar, loc. cit.; B. N. Desai and A. K. Desai, loc. cit ) that (i) for samples of sol dialysed for periods shorter than what corresponds to the maximum in the C. S.—D (dialysis) curve, on diluting the sol, the cataphoretic speed of colloidal particles first increases, reaches a maximum value and then decreases and (ii) for samples of sol dialysed for longer periods, the cataphoretic speed regularly decreases on dilution of both the sols.

18. Both on diluting and dialysing the sol the amount of the peptising electrolyte decreases. The processes of dilution and dialysis can therefore be considered similar in this respect. Now as shown in section (c), if a colloidal solution initially contains an amount of the peptising electrolyte more than what corresponds to the maximum in the C. S.—C curve the cataphoretic speed first increases and then decreases on dialysis. The samples of the sol dialysed for periods shorter than what correspond to maximum in the C S.—D curve do contain an amount of the peptising electrolyte which will be more than what corresponds to the maximum in the C S.—C curve and therefore the processes of dilution and dialysis being similar, the cataphoretic speed should first increase and then decrease on dilution of the sol. Sols dialysed for longer periods than what corresponds to the maximum in the C S.—D curve should show on diluting, a continuous decrease in the cataphoretic speed as they contain an amount of the peptising electrolyte less than what corresponds to the maximum in the C. S.—C curve, for such samples the cataphoretic speed also regularly decreases on dialysis.

19. If the analogy between processes of dialysis and dilution given in the preceding paragraph is correct, one should expect that the maximum in the C.S.—Dil (dilution) curve should occur at lower dilutions in the case of sols dialysed for longer periods than those dialysed for shorter periods. This has actually been found to be the

case (Desai and Borkar, loc. cit. and B. N. Desai and A. K. Desai, loc. cit.). In what respects dialysis and dilution cannot be considered similar has also been discussed by Desai in the above papers. It is however considered that changes in cataphoretic speed on dialysis and dilution are mostly due to changes in the concentration of the peptising electrolyte. Different sols are being investigated to see how far observations (i) and (ii) given in para. 17 are also noticed in them in order to find out if this behaviour is a general property of colloidal solutions.

20. On diluting the sol the stability as determined by the F.V with KCl decreases regularly for both ferric and thorium hydroxide sols. As shown in para. 16 there does not appear a direct relation between charge and stability in all the cases, for, as stated above, the changes in the cataphoretic speed on dilution are not the same for sols dialysed for different periods.

21. Dhar (for references see Desai, Kolloidchem. Beihefte, 26, 385, 1928) has divided colloidal solutions into two divisions according as they show normal or abnormal behaviour to the dilution rule, *vis.*, the greater the concentration of a colloid the greater the amount of an electrolyte necessary for coagulation. According to Dhar, only those sols show an abnormal behaviour to dilution rule which show appreciable preferential absorption of similarly charged ions from the solution. Desai (above quoted paper) has however shown that colloidal thorium hydroxide can be made to show either normal or abnormal behaviour to dilution rule by varying the purity of the sol (by subjecting the sol to dialysis), and that it is erroneous to divide the colloidal solutions into two classes as done by Dhar. We have also observed that both colloidal ferric and thorium hydroxide show appreciable preferential adsorption of K ion in the presence of KCl (Desai and Borkar, loc. cit, B. N. Desai, and A. K. Desai, loc cit.), and that both these sols show normal behaviour to dilution rule when they are coagulated with KCl. Thus Dhar's explanation about abnormal behaviour to dilution rule also does not seem to be correct

22. In explaining the abnormal behaviour to the dilution rule, it has also been stated that a dilute sol adsorbs proportionally more of the similarly charged ion than the concentrated one. Our preliminary results (Desai and Barve, Nature, 128, 907, 1931) have shown that on the addition of small increasing amounts of KCl and  $MgCl_2$ , the cataphoretic speed first increases and then decreases, the initial increase being greater with the concentrated sol than with the dilute sol. It was also observed that the maximum value of cataphoretic speed occurs at a lower concentration of the electrolyte in the case of dilute sol than the concentrated one. These results thus do not support the conclusion that there being greater adsorption of the similarly charged ion in a dilute sol than a concentrated one, the charge will be greater in the

former case and hence a greater amount of electrolyte will be required for coagulation. Also the explanation for disappearance of abnormality to the dilution rule, as in the case of the Schulze-Hardy law, with the progress of dialysis should be modified as indicated in para. 11. It appears that increase in distance between colloidal particles on dilution, might have considerable influence on the coagulation and make the sol show an abnormal behaviour as regards stability (cf. Desai, *Kolloidchem. Beihefte*, 26, pp. 400-401, 1928).

(e) *Relation between charge and viscosity.*

23. There are two different views at present about relation between charge and viscosity. According to v. Smoluchowski (for references on this subject see papers by Desai and Borkar, loc. cit.; B.N. Desai and A K. Desai, loc. cit.) the movement of electrically charged particles of a sol causes the development of an electric field, which hinders the flow of the sol resulting in an increase of its viscosity. This conclusion was found to be supported by Smoluchowski's measurements which showed that a sol containing particles of greater electric charge was more viscous than a sample containing particles of feeble electric charge. On the other hand, Dhar and co-workers from their measurements with a number of sols have tried to show that the view of Smoluchowski is untenable. According to them, other things being identical, a decrease in the electric charge on colloidal particles causes an increase in hydration and necessarily in the viscosity of the sol. It should however be stated that Dhar's conclusions about changes in charge are based on F.V determinations and this is certainly not correct in view of what has been said in the foregoing sections about relation between charge and stability as determined by F.V.

24. We have made simultaneous measurements of charge and viscosity of colloidal solutions of ferric and thorium hydroxide dialysed to different extents and of different concentrations and in the presence of varying amounts of electrolytes. In the case of colloidal ferric hydroxide we have observed (Desai and Borkar, loc. cit.) that

(i) With the progress of dialysis, cataphoretic speed first increases and then decreases, while viscosity first decreases and then increases. The maximum in the C.S.—D curve and the minimum in the V (viscosity)—D curve however do not occur at the same stage of dialysis.

(u) On adding small increasing amounts of electrolytes with univalent coagulating ion, cataphoretic speed first increases and then decreases, while viscosity first decreases and then increases. The maximum in the C.S.—C curve and the minimum in the V—C curve do not however occur at the same concentration of the electrolyte.

(iii) With highly concentrated sols of  $\text{Fe}_2\text{O}_3$ , the initial decrease

in viscosity with the progress of dialysis is not noticed at all (Desai, Special Number of the Journ. Indian Chem. Soc p. 37, 1933).

In the case of colloidal thorium hydroxide we have observed (B.N. Desai and A.K. Desai, loc. cit.) that

(i) With the progress of dialysis, cataphoretic speed first increases and then decreases, while viscosity continuously increases—the increase being more marked in the later stages of dialysis.

(ii) On diluting the sol cataphoretic speed first increases and then decreases for samples which have been dialysed for periods shorter than what corresponds to the maximum in the C.S.—D curve and it continuously decreases on dilution for samples which have been dialysed for longer periods. Viscosity, on the other hand, continuously decreases on dilution in all the cases although the samples of sol were dialysed to different extents. Also the percentage increase of viscosity on dialysis is greater in the case of concentrated sols than dilute sols.

(iii) For all the samples of the sol, whether dialysed for short or long periods, cataphoretic speed first increases and then decreases on the addition of small increasing amounts of electrolytes having univalent coagulating ion, the initial increase in cataphoretic speed being not noticeable with electrolytes having bivalent coagulating ion. Viscosity, on the other hand, increases continuously with all the electrolytes for samples of the sol which have been dialysed for periods shorter than what corresponds to the maximum in the C.S.—D curve, while for samples dialysed for longer periods the viscosity first decreases and then increases on adding small increasing amounts of electrolytes to the sol.

25. It will appear from the above results that neither the view of Dhar nor of v. Smoluchowski can alone explain the changes in charge and viscosity of colloidal ferric and thorium hydroxide under different conditions—with the progress of dialysis, with a change in dilution and when small increasing amounts of different electrolytes are added. As pointed out in our papers one has to consider the effect of various factors, which are given below, in explaining these changes in charge and viscosity.

(i) Changes in the concentration of disperse phase.—The viscosity of the sol will generally decrease with a decrease in the concentration of the disperse phase.

(ii) Electro-viscous effect.—The viscosity of the sol will increase with an increase in the cataphoretic speed of colloidal particles and decrease when the cataphoretic speed decreases.

(iii) Changes in hydration of colloidal particles.—With an increase in hydration of the colloidal particles (this tendency is most pronounced with the progress of dialysis when the sol shows a tendency to set to gel) the viscosity will also increase, there being an increase in

the effective volume of the particles. On diluting the sol, the hydration of colloidal particles may increase and the viscosity may also increase due to an increase in the effective volume of the particles.

(iv) Variation in the shape and structure of particles.—As for the variation of the shape of the particles little is known. However the structure of the particles is sure to vary both during dialysis and dilution. During dialysis, there is a tendency for the particles to aggregate as during coalescence and thus increase their effective volume and the viscosity. On the other hand, on dilution the larger aggregates may break up into smaller ones and thus decrease the effective volume of the particles as well as viscosity.

(v) Changes in the concentration of the electrolyte.—The viscosity will increase regularly with an increase in the concentration of the electrolyte present in the sol except with those electrolytes which show a negative viscosity within a particular range of concentration.

26. In a previous paper Desai (*Kolloidchem. Beihefte*, 26, 422, 1928) has explained changes in viscosity on dialysis and ageing by assuming that as with the progress of dialysis and on ageing, the sol becomes unstable, the charge decreases and therefore viscosity increases. In view of what has been said in previous sections it is not right to draw conclusions about changes in charge from stability determinations and therefore the above explanation may have to be considerably modified. The influence of all the factors mentioned in the previous para. should be taken into account. As the ceric hydroxide sol initially contains quite a large amount of the peptising electrolyte it is likely that on dialysing, the charge on colloidal particles may first increase and then decrease as in the case of ferric hydroxide and thorium hydroxide sols. The changes in the various properties of colloidal particles of ceric hydroxide under different conditions are being investigated.

27. In a recent paper Ghosh and Banerji, (*Bul. Acad. Sci. U. P.*, 2, 135, 1933) have given some measurements of viscosity of colloidal ferric phosphate dialysed and diluted to different extents, the flow of the liquid being caused under varying pressure. They have stated that if measurements of rates of flow of a colloid be undertaken at fairly high pressures, the change in the viscosity of colloids with the progress of dialysis will be either nil or insignificant. According to them hydration has to be assumed to be very labile. Our results of study (Desai, loc. cit.) of the ceric hydroxide sol and gel also seem to support the conclusion about labile nature of hydration. Ghosh and Banerji however believe that colloidal solutions show a high viscosity due to an orientation of the particles rather than due to high hydration of the disperse phase. According to them the tendency to orientation increases as the electric charge on the colloid particles is decreased and

as, during dialysis, the electric charge on colloidal particles continuously decreases the viscosity will increase. It should be pointed out here that their conclusion about changes in charge during dialysis is based on coagulation experiments as they themselves state. This is not justified in view of what has been stated in previous sections about changes in charge during dialysis. In fact the ferric phosphate sol which they have used initially contained a considerable amount of the peptising agent and therefore the charge on colloidal particles during dialysis will first increase and then decrease instead of continuously decreasing as shown by stability determinations. Our examination of ceric hydroxide gel under ultra-microscope (Desai, loc. cit.) has revealed no tendency for a definite orientation of the particles in that gel. Our gel contained more than 2000 mols of water per one mol of  $\text{CeO}_2$  (the amount of water depending on temperature of gel formation) and it is considered that a considerable increase in viscosity during dialysis is due to an increase in hydration of the particles. Also the decrease in viscosity under high pressures noticed by Ghosh and Banerji (loc. cit.) is not due to a destruction of the orientation of colloidal particles under high pressures as supposed by them, but definitely due to a decrease in the hydration of the particles on account of some water molecules wrapping the particles having been torn off and the effective volume of the particles having thus been decreased. It is not necessary to consider that increase in hydration is as a result of adsorption of water by colloidal particles, for large amount of water held by the gel will demand adsorption several molecules deep and this is incompatible with Langmuir's theory (J. Amer. Chem. Soc., 38, 2221, 1916; 40, 1361, 1918), according to which the adsorbed layer cannot be several molecules deep. The picture of hydration suggested by Desai (Kolloidchem. Beihefte, 26, 434, 1928) will easily allow some water molecules being torn off under high pressures and thus explain the decrease in viscosity with an increase in the shearing force. There is also no evidence to suppose that orientation of colloidal particles in a sol changes during dialysis.

28. In view of what has been stated in this section it will be clear that it is erroneous to draw conclusion about changes in charge from changes in viscosity as in the case of stability (para. 16), and that there is a necessity to study simultaneously changes in charge and viscosity of colloidal solutions under different conditions. This is being done in our laboratory.

(f) *Sensitisation of colloidal solutions by non-electrolytes.*

29. We (Patel and Desai, Kolloid Zeit., 51, 318, 1930) have studied the influence of non-electrolytes—methyl, ethyl and iso-propyl alcohols, acetone, urea and cane-sugar on the rate of coagulation of



colloidal thorium hydroxide of different degrees of purity in the presence of NaCl, the coagulation of the sol in the presence of non-electrolytes alone has also been studied. The following results have been obtained.—

(i) With the progress of dialysis the sol is more and more sensitised by non-electrolytes.

(ii) A fairly pure sample of the sol (sol dialysed for 6, 8 and 11 days) could be coagulated by non-electrolytes alone, the coagulating power of non-electrolytes increasing with an increase in the purity of the sol.

(iii) The C. V. curves for lower concentrations of electrolytes and non-electrolytes or non-electrolytes alone are found to be S-shaped. The S-shape of the C. V. curves becomes less marked with an increase in the purity of the sol.

(iv) The order of effectiveness in sensitisation or coagulation of the sol by the non-electrolytes tried in these experiments is

Urea > methyl alcohol > ethyl alcohol > iso propyl alcohol > cane-sugar > acetone.

30. The view of Weiser (J Phys Chem., 28, 1253, 1924) that sensitisation is caused due to the cutting down of the adsorption of the coagulating ion in the presence of non-electrolytes is not applicable in the present case because the C. V. increases in the presence of non-electrolytes. Also the fact that fairly pure samples of the sol could be coagulated with non-electrolytes alone shows that the above view is not of much help in explaining our results.

31. The other view of Weiser (loc cit.) that the non-electrolytes displace the stabilising ion is supported by our results. For, such a displacement of the stabilising ion will make the sol unstable and if stability is defined in terms of coagulation concentration, smaller amounts of electrolytes will be required to coagulate the sol in the presence of non-electrolytes. This view will also explain the coagulation of the sol by non-electrolytes alone, for if the non-electrolytes are able to displace so much amount of the stabilising ion from the inner sheet of the double layer that the value of the charge on the particles is lowered to the critical value, the sol will begin to coagulate—slow coagulation phenomenon. If the amount of the stabilising ion displaced is quite considerable the value of the charge on the colloidal particles may be brought down to the iso-electric point and the coagulation may become rapid from the beginning. It should however be stated that it is not possible to say how far the displacement of the stabilising ion by the non-electrolytes will be shown by actual adsorption experiments.

32. The suggestion of Wo. Ostwald (Grundriss der Kolloid Chemie, 1 Aufl. 1909. p. 441) and of Freundlich (Colloid and Capillary

Chemistry. Eng. Translation, 1926, pp. 462-65) that changes in the dielectric constant decide the influence of non-electrolytes is found to be supported by these experiments. All the non-electrolytes tried in our measurements had dielectric constant lower than that of water and therefore if the non-electrolytes are adsorbed in the double layer the dielectric constant will be lowered and with it the electric charge on the colloidal particles. Whether there will be slow or rapid coagulation in the beginning will depend upon the extent of the lowering of the charge.

We have observed that with the progress of dialysis the charge on colloidal particles of thorium hydroxide first increases and then decreases. If the coagulation by non-electrolytes is due to a lowering of the dielectric constant and hence of the electric charge, one would expect that the samples of the sol having the same cataphoretic speed *s. s.*, on the one or the other side of the maximum in the C. S.-D curve should show the same behaviour when non-electrolytes are added. It will however be seen from our results that the sol could be coagulated with non-electrolytes alone only when it was dialysed for long periods (6, 8 and 11 days); sols dialysed for shorter periods *s. s.*, less than what corresponds to the maximum in the C. S.-D curve (sols dialysed for 0 day and 3 days) could be only sensitised but not coagulated by non-electrolytes alone. It thus appears that the non-electrolytes are not able to lower the dielectric constant as much in the presence of appreciable amounts of electrolyte (sols dialysed for 0 day and 3 days certainly contain quite appreciable amounts of the stabilising electrolyte when compared with samples dialysed for 6, 8 and 11 days) as they can do in their absence, or that the adsorption of the non-electrolytes in the presence of electrolytes is not quite appreciable. A tendency to this effect is noticeable somewhat in the results of Mukherjee, Rai Choudhuri and Rao (J. Indian Chem. Soc., 5, 697, 1928). This point however requires further investigation.

The results of Mukherjee and co-workers (*loc. cit.*) show that the cataphoretic speed of colloidal particles of arsenious sulphide is lowered more and more on adding larger and larger amounts of non-electrolytes which also sensitise the sol. It is therefore quite likely that even in the case of thorium hydroxide addition of non-electrolytes which sensitise the sol will lower the cataphoretic speed. This work is in progress.

33. Mukherjee and co-workers (*loc. cit.*; J. Indian Chem. Soc., 2, 307, 1925; 3, 349, 1926) consider that the diminution in the dielectric constant brings about two effects:—

(i) The electrical work, resulting from the displacement of the ions constituting the mobile sheet of the double layer and surrounding the colloidal particles, when two particles approach sufficiently near

each other, will increase with a diminution of the dielectric constant. This effect will decrease the rate of coalescence and tend to stabilise the sol.

(ii) From Mukherjee's theory of the electrical adsorption of the precipitating ions it follows that the adsorbability will increase in a medium of low dielectric constant. This effect will give sensitisation. The net effect will depend on the relative magnitudes of factors (i) and (ii).

In our case the effect of factor (i) has been either absent or less predominant than the effect of factor (ii) because stabilisation of the sol did not take place in any experiment. Factor (ii) can be utilised to explain both sensitisation and coagulation of the sol by non-electrolytes.

Mukherjee and co-workers (loc. cit., also Choudhury, J. Phys. Chem., 32, 1481, 1928; Special Number of J. Indian Chem. Soc., 201, 1933) have also suggested that variation in the thickness of the double layer, changes in the interfacial tension of the medium etc., take place in the presence of non-electrolytes. It should however be stated that in the absence of any definite knowledge of variation of the above properties of the double layer it is not quite correct to use these factors in explaining the results of sensitisation by non-electrolytes (cf. Weiser, J. Phys. Chem., 44, 101, 1930). It appears that the role of dielectric constant in the sense proposed by Wo. Ostwald and Freundlich may, to a very large extent, explain the results of sensitisation, although in some cases some other influences may have also to be taken into account.

34. In a recent paper Prasad and Nabar (J. Indian Chem. Soc., 10, 53, 1933) have studied the influence of non-electrolytes on the coagulation of colloidal ceric hydroxide by the thermopile method. They find that alcohols affect the stability with the progress of dialysis of the sol in the same manner as observed by Patel and Desai (loc. cit.) in the case of thorium hydroxide sol, sugars are however found to stabilise the ceric hydroxide sol and this effect increases with the progress of dialysis. The stabilising effect of sugars in this case may be due to the effect of factor (i) discussed in para. 33 as well as due to the cutting down of the preferential adsorption of the coagulating ion by the sugars. Regarding Prasad and Nabar's results it must be stated that in explaining their results they have assumed that the charge decreases regularly with the progress of dialysis. This is not justified in view of the fact that their sol contained initially appreciable amount of the peptising agent and therefore during dialysis the charge may first increase and then decrease.

#### CONCLUSION.

35. From the foregoing considerations it is apparent that changes which will be produced in the charge on colloidal particles during

dialysis are not so simple as many colloid chemists seem to imagine. It will also be clear that the results of viscosity and stability (towards electrolytes and non-electrolytes) cannot always be utilised for getting an idea about charge on colloidal particles. Under the circumstances it is difficult to understand how far one should consider as satisfactory the interpretations of the results of coagulation of colloids or of viscosity determinations whenever inferences have been drawn from them about changes in charge on the particles. There is thus a clear necessity of investigating simultaneously different properties of various colloidal solutions—cataphoretic speed, stability, viscosity etc.,—which have been dialysed to different extents in order to get a clear idea about relation between various properties.

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*Note*—Paper by Desai and Borkar on Ferric Hydroxide referred to in para 6 has appeared in the December 1933 number of the *Transactions of the Faraday Society*, London.

## SMOKE AND ITS PREVENTION

By

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Industrialism is rapidly spreading over our Indian cities which congested and crowded as they are, have already begun to feel the effects of mechanization and of comparatively large scale production.

Among the many problems which follow in the wake of industrial progress, is the abatement of smoke and dust and the taking of measures against atmospheric pollution.

In almost every city, where hydro-electric power is not available, coal is the chief source of generating electrical energy, supplying heat and producing steam and power. The boiler plant whether large or small is also invariably associated with factories, marine vessels, locomotives, trucks, cranes, shovels, steam rollers etc., and the general indication of such boiler plants in operation is the black smoke and dirt belching forth from their chimneys or stacks.

From the standpoint of hygiene, aesthetics and economics, it is highly desirable if not essential that the occurrence of smoke should be prevented and the air kept as free from dust as possible.

It is the primary concern of Municipalities to see to public health. Our markets are kept clean and we are supplied with pure, filtered, drinking water. The average individual is rather careful about clean food and water but how about the air that he or she inhales? The normal consumption of solids and liquids by the human system is about  $5\frac{1}{2}$  pounds in 24 hours but the air breathed, is over 35 pounds in the same period. One can imagine how harmful could the impurities in so much air be to the lungs and the chest. Is it not a logical step to legislate and make regulations in order also to prevent people from introducing obnoxious fumes, smoke and grit in the atmosphere which surrounds urban communities?

Of the industrial dusts, smoke and Municipal dust are no doubt harmful but far more serious problems are connected with industries such as granite quarrying in which the employees have to suffer from a dust concentration 40 times as much giving rise to such diseases as silicosis and consumption. However, as city atmosphere affects a large number of people, and as it actually pays not to have smoke, the subject should receive careful attention from the public at large.

Nuisance due to dust particles, spoiling of the aesthetic features of landscapes and residential quarters on account of unsightly streaks of smoke and the fouling of buildings, paintings, silverware, furniture etc., are sufficient reasons for passing legislation against smoke emission. It is estimated that in the city of New York, the damage caused by smoke amounts to the appalling figures of over Rs. 50 per annum per head. No wonder that of late there have been so many questions raised in the British Parliament to replace bituminous coal by some sort of smokeless fuel.

As far as the consumers of coal are concerned, they would have enough inducement to keep the smoke down if they only realize that smoke abatement also entails economy in fuel. It is only due to lack of knowledge and want of engineering skill that they unnecessarily lose money by continuing antiquated methods.

Smoke is the direct result of improper combustion or the burning of coal. To burn a shovelful of coal (say about 20 lbs. or 0.4 cu. ft.) it requires as much air as would be contained in a room 16' x 16' x 16' (nearly 4,000 cu. ft.). From these proportions it may readily be observed that to thoroughly burn coal, enough air and proper contact are necessary. A little consideration will show that this is not so easy when coal is fired in a haphazard manner.

Visible smoke mainly consists of minute particles of carbon, tar and ash carried away by the products of combustion which are carbon-dioxide, water vapour and carbon monoxide with traces of hydrocarbons (due to incomplete combustion) together with the inert nitrogen of the air. Microscopic analysis shows that these particles are composed of groups of still smaller particles about two millionth part of an inch in diameter!

The actual loss of carbon in dense smoke amounts to about 1% of the carbon in the coal but in terms of heat units this loss itself is only about 3 to 4%. It is the loss of heat units in the accompanying carbon monoxide and hydrocarbons that is so serious and may amount to nearly 15% of the heating value of coal. It should be remembered, therefore, that when you see smoke, you actually visualize only a fraction of the total heat loss.

To make it more clear let us consider the combustion of a pound of carbon. If it is so burnt as to give only carbon monoxide instead of carbon dioxide, then we lose 10,600 B. Th. U.'s or a quantity of heat which could evaporate  $3\frac{1}{2}$  times as much water at 212°F. as is possible to generate from the heat of formation of carbon monoxide.

In the case of boiler practice, insufficient or sufficient (i. e. 40 to 50% excess) air might make a difference of as much as 10 to 15% in the cost of steam generation.

Now, coal is not a homogeneous substance. It is composed of hydro-carbons, carbon, ash and moisture, and when subjected to heat,

its volatile matter is first driven away leaving behind carbon mingled with ash which is called coke. Consequently, for combustion, air has to be so regulated as to first thoroughly burn the gaseous products which leave the coal as soon as it gets heated. When air is insufficient, the volatile matter instead of being thoroughly burnt, cracks up forming soot and other hydro-carbons of a more stable nature. Hence, lack of air is the primary cause of smoke.

The second cause may be put down as due to either too low or, too high a combustion chamber temperature. If the temperature is too low (as in the case of furnaces starting up) the fuel is not properly ignited and the gases leave the furnace decomposed and sooty. When the temperature is too high the heavy hydrocarbons and tar break up into soot in about a tenth of a second, *i. e.*, too quickly to enable air to react with them. Soot once formed is difficult to burn and flies up the chimney as smoke.

The third and general cause of smoky stacks is the improper design of furnaces. In most cases the combustion space is far too small to allow sufficient time for the gases and air to react. In others, the grate or burner construction is such that proper mixture and intimate contact of fuel and air are lacking.

The prevention of smoke, therefore, depends on the proper application of the general principles of combustion. It is worthwhile therefore to look into a few practical methods which are useful in ensuring thorough combustion.

When dealing with hand fired furnaces, only skilled firemen should be kept on the job. Small quantities of coal must be charged at a time as frequently as necessary and first allowed to coke on the plate in front of the grate. During the time that the gases distil off the charging door should be left ajar to let in plenty of secondary air. This is the first step taken in order that the hydrocarbons may be thoroughly burnt. The second step which consists of pushing the fuel on to the grate allows the coke to be uniformly fired with a set quantity of air.

In the case of larger units, the selection of a suitable stoker must not be overlooked.

There are many types of stokers and salesmen have a tendency to offer this important equipment without advising as to its suitability for a particular grade of coal. Stoker and furnace construction meant for a low volatile coal turns out to be inefficient when it is used for the firing of high volatile coal. Smokeless settings, well-designed arches and proper baffling to suit particular conditions, are highly important factors and money spent in rebuilding furnaces certainly is repaid.

Varying or excessive loads are often the cause of smoke from the stacks of even well-designed boiler furnaces and operation should be

more uniform. The forcing of boilers is a bad practice.

In the smaller units, lack of draft and turbulence are sometimes overcome by the use of steam jets by which means air can be injected into the furnace usually above the firing door. This practice may be resorted to only in cases where there is no other solution to the problem.

When the question of new installation arises, pulverised coal fired furnaces should be given serious consideration.

The more up-to-date plants have automatic combustion control devices, carbon-dioxide recorders, air preheaters and sometimes out of necessity they are equipped also with flue dust extraction devices.

The problem does not end with smoke abatement only. A lot of fly ash and dust escapes through the chimneys of large power stations (mostly those which operate on powdered coal) and settles down miles around in the surrounding district. When people not only demand relief from smoke but also agitate for freedom from dust and fumes it becomes a serious problem as considerable expense has to be incurred in providing dust extraction plant

The types of dust extraction plants, commonly used in Europe, are (a) water film and spray (b) cyclone and (c) electrostatic. The capital costs of the water film and spray and multicyclone types are about the same and only about half the capital cost of the electrostatic plant. The total cost (including the fixed charges) of removing flue dust is very nearly the same for the three processes. The electrostatic precipitator though somewhat more expensive is said to have a high efficiency (90 to 95%) and has the advantage of separating out the dust in a dry form.

In cities where there are numerous factories located within limited areas, a drive should be made towards centralising the power plant. A large central power station would not only supply power cheaply but would also prevent smokiness by replacing a number of small inefficient units.

In England several attempts to prevent smoke have been made since the 14th century or still earlier. Numerous ordinances have been passed and committees appointed.

In recent years organised efforts have succeeded in greatly reducing smoke in some of the American cities. Smoke inspectors have been appointed and special regulations framed. If smoke of a certain density appears from a stack for a longer period than that specified, the ordinances are put into force. Qualitative smoke determinations are made ordinarily using the Ringelmann charts. These are large charts each cross ruled with lines of a certain thickness so that when placed at a certain distance from the observer, they appear of four shades intermediate between a white chart and a totally black one.



The colour density of smoke is then judged by comparing it with the charts.

In conclusion, it must be said that there is every justification to agitate for legislation for smoke and dust abatement in the interests of hygiene and economy. With our present knowledge of the scientific utilization of fuel, there should be little difficulty in ridding big cities like Bombay, Ahmedabad, Nagpur and Calcutta of the smoke nuisance.

## RECENT WORK ON ANTIMALARIALS

By

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During the last fifteen years, a large amount of work has been carried out on the chemotherapy of malaria. Systematic investigations have been made on the relative values and limitations of the cinchona alkaloids, which still hold the field in the treatment of malaria, in spite of many attempts to replace them by the so called "modified alkaloids" or synthetic compounds. Attempts only in part successful, have also been made to correlate chemical constitution and antimalarial activity. The discovery in 1926, of "plasmoquin," a synthetic quinoline derivative which has been found to be of great value in treatment of human malaria, is an outstanding achievement of chemotherapeutic investigation, and has stimulated attempts to prepare synthetic antimalarials.

The first systematic use of cinchona bark as an antipyretic is due to Juan del Vego, physician attendant to the Countess Anna del Chunchon, wife of the Governor of Peru, who introduced the bark into Spain for treating agues on his mistress's estates, in or about 1639.

In 1820, Pelletier and Caventou in Paris isolated from the bark two alkaloids which they named quinine and cinchonine. Cinchonidine and quinidine were isolated thirtytwo years later.

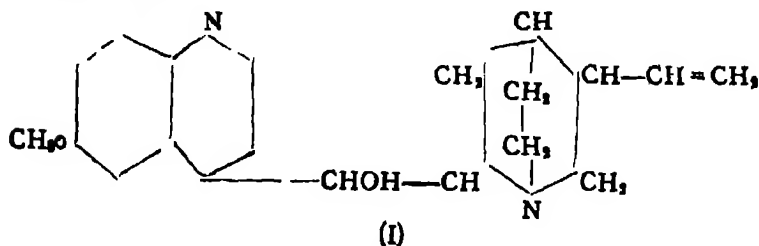
About 1860, attempts were made to introduce cinchona trees in India, Ceylon, Jamaica, Australia and Java, but success was attained only in India and Ceylon. Of late years, cinchona cultivation has declined in these countries, and has immensely increased in Java, which is now the most important cinchona district in the world. This is due to the extensive botanical and chemical investigations relating to the cinchona cultivation which have been carried out under the auspices of the Dutch East Indian Government.

The five chief crystallisable alkaloids present in cinchona bark are quinine, quinidine, cinchonine, cinchonidine, and hydroquinine, there are also present about twenty other alkaloids in smaller quantities which are non-crystallisable and amorphous.

While all these alkaloids have been known for long to possess antimalarial properties, there was no general agreement regarding their relative efficacies. Goodson, Henry and Macfie<sup>1</sup> who have recently reinvestigated this problem, using alkaloids of undoubted purity and

more refined technique for biological tests, conclude that hydroquinine is the most effective, the remaining four being approximately of equal value.

The chemical constitution of quinine is represented by (I). It is thus p-methoxy-y-quinoyl-β-vinyl-2-quinuclidyl-carbinol, the two component rings being called the quinoline and the quinuclidine residues. Quinidine is a stereoisomeride of quinine, and hydro-quinine contains the saturated ethyl ( $-\text{CH}_2-\text{CH}_2$ ) group in place of the vinyl ( $-\text{CH}=\text{CH}_2$ ) group of quinine. Cinchonine and cinchonidine which are stereoisomerides only differ from quinine in the absence of the methoxyl group.



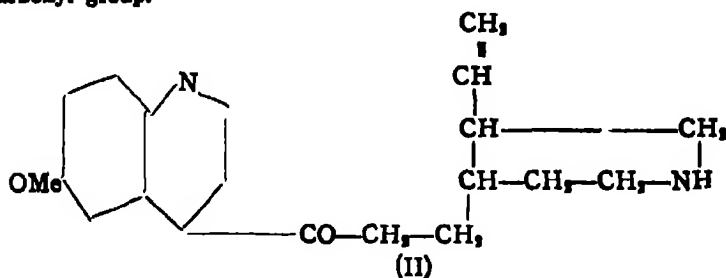
Detailed study has been made of the physiological action of quinine, which is found to have a strongly antipyretic action, and bactericidal, narcotic and local anæsthetic action, in varying degrees.

Attempts which have been made to ascertain the particular molecular arrangement present in these alkaloids which is responsible for their biological activity, have given results which are rather vague and indefinite. It appears that the quinoline methoxyl contributes to a small extent to the antimalarial activity. Hydrogenation of the vinyl group of the quinuclidine ring gives methyl hydrocupreine which is as active as quinine, but more toxic. The dehydrocompound from quinine containing the group  $-\text{C}\equiv\text{CH}$  in place of  $-\text{CH}=\text{CH}_2$  is only half as active. The conversion of the  $-\text{CH}=\text{CH}_2$  group to  $-\text{CHOH}-\text{CH}_2$  by the addition of water across the double bond leaves the activity unchanged. The rearrangement of the vinyl group to the  $=\text{CH}-\text{CH}_2$  group gives the interesting compound isoquinine which is as active as quinine, although a little more toxic.

Other points of the variation of the quinine molecule have also been investigated. The oxidation of the secondary alcoholic group gives ketoquinine, while reduction to  $\text{CH}_2$  gives the methylene compound, cinchene, which is extremely toxic producing tetanus and death. Fracture of the quinuclidine ring yields quinacine (II) which is highly toxic, being a strong convulsant, and fatal in larger doses.

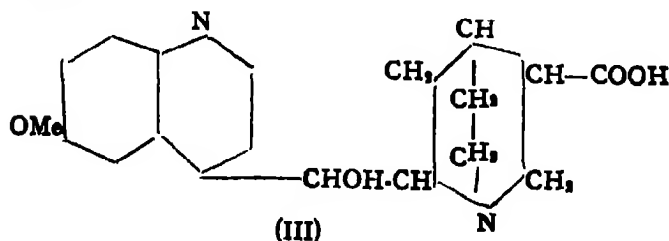
Little information has been made available regarding the simple quinoline derivatives, whereas simple quinuclidine compounds do not

seem to have been investigated. Strangely enough, the antipyretic action of p-methoxy quinoline is less than that of quinoline itself, whereas p-methoxy quinoline- $\gamma$ -carboxylic acid is almost completely inactive, as might be anticipated from the presence of the deactivating carboxyl group.



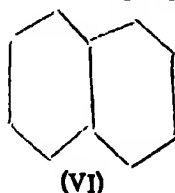
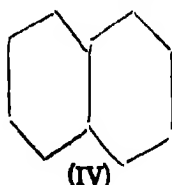
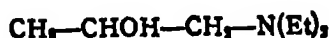
Earlier attempts at preparation of anti-malarials were made by modifying the structures of cinchona alkaloids. The so-called "modified alkaloids" which were investigated were the carboxylic acids produced by the oxidation of the  $-\text{CH}=\text{CH}_2$  (vinyl) group of the cinchona alkaloids to the  $-\text{COOH}$  group and their esters.

Thus quinine, quinidine, cinchonine, cinchonidine gave quintanine, quitenidine, cinchotenine, and cinchotenidine. Quitenine (III) is found to be inactive but according to Geisma, Weise, and Tropp,<sup>2</sup> the activity is regained in the ethyl ester called ethyl-quitene on esterification of the carboxyl group with ethyl alcohol. The methyl, propyl and other alkyl quitenines have also been examined, and the interesting generalisation has been drawn that antimalarial activity increases as the homologous series is ascended, reaching a maximum at butyl or amyl. Similar relationships appear to hold good in the cases of the esters of cinchotenidine, quitenidine, and cinchotenine. However none of the compounds approaches quinine in efficiency against bird malaria.

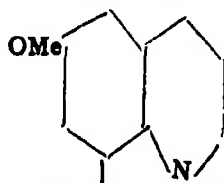


Proceeding on the assumption that the secondary alcoholic hydroxyl group of quinine is essential for antimalarial activity Forneau and collaborators<sup>3</sup> have prepared a number of relatively simpler aminalcohols of the naphthalene series like (IV), (V) and (VI) of which some

like (V), and (VI) were active against bird malaria but inactive against human malaria.



A new and most promising clue in the search for synthetical anti-malarials has been provided by the discovery in 1926 of plasmoquin, a synthetic quinoline derivative. The structure of the drug is not known with certainty, but according to Hörlein, the director of the pharmaceutical department of the I. G. Farbenindustrie, the compound is N-diethylamino-isopentyl-8-methoxy quinoline (VII), thus differing from quinine chiefly in the absence of the quinuclidine nucleus with the two intermediate methylene groups.



First biological experiments were carried out with the new compound on the parasites of bird malaria, in the case of canaries which were found to be most suitable for the purpose by Roehl. The experiments were then extended to human malaria, in which some success was achieved. Although the high hopes entertained for

plasmoquin in the beginning have not been fully realised, it is a compound of great value in the treatment of malaria in human beings.

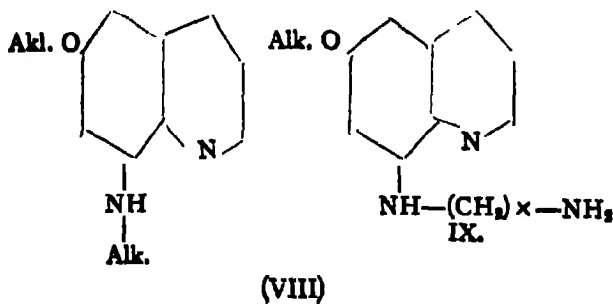
The antimalarial effects of plasmoquin were first demonstrated by the use of Roehl's technique, which depends on the fact that it is possible to infect birds with plasmoquin relictum, thus communicating to them a malady, the evolution of which resembles that of human malaria.

By means of this new procedure, the activity of a synthetic compound can be so easily tested that it may be hoped that plasmoquin is but the first of a series of still more efficient antimalarials to be discovered in future.

Since the discovery of plasmoquin, which apart from the cinchona alkaloids is the only known compound which has shown promise in the treatment of human malaria, it has been largely adopted by subsequent workers as model upon which to base the synthesis of new compounds.

In England, systematic research on synthesis of new antimalarials, planned as a campaign against malaria, has been initiated by Barger and Robinson,<sup>6</sup> with the co-operation of the joint Committee on Chemotherapy formed by the Medical Research Council and the Department of Scientific and Industrial Research, and a number of new compounds of possible antimalarial activity have been made to which a brief reference may be made.

Aminoalkyl quinolines of the types (VIII) and (IX) bearing structural resemblance to plasmoquin, have been synthesised by Baldwin,<sup>8</sup> and aminoalkylquinolinium salts by Sheshadri.<sup>6</sup> Kermack and Smith<sup>7</sup> prepared 4-piperidino- and 4-piperazino-2-methyl quinolines, while Kermack and Muir<sup>8</sup> have extended the work by substitution of a more complex sidechain containing two nitrogen atoms in place of the simple piperidine or piperazine ring. Of a different type are the pyrrole-quinolines obtained by Mrs. Robinson,<sup>9</sup> showing similarity to the alkaloids harmine and harmaline, which are known to possess antimalarial action.



It is gratifying to note that some work in this direction has also been done in India.

J. N. Ray and collaborators<sup>10</sup> have synthesised several compounds amongst which are a glyoxalino-quinoline, pyrrol-indoles, and condensation products of cotarnine and phenols.

Brahmachari and coworkers<sup>11</sup> have prepared a number of quinoline derivatives including dimethyl-amino-styryl-quinolines, quinoline-amido-acetamides, carbamido-quinolines, quinoline-amino-acetyl-p-arsenilic acids and 8- $\beta$ -aminoalkyl-amido-quinolines.

As the results of the biological tests on the therapeutic activities of many of the synthetic compounds referred to in the article, are not yet published, it is not possible at this stage to make any generalisations.

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## ABSORPTION OF LIGHT IN POLYATOMIC MOLECULES

*By*

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Studies in the absorption spectra of solutions in the ultra violet and the visible region of the spectrum have yielded results which are of great importance to the chemist, inasmuch as they have given sufficient clues to decide between possible alternatives in the structure of complex organic molecules. Such studies have often been employed in the identification and purification of certain organic compounds. A detailed knowledge of the light absorption in various substances has also proved useful in devising light filters for the isolation of various radiations in the different parts of the spectrum. Besides these practical applications, on the theoretical side observations on the absorption spectra of a large number of coloured and colourless compounds have enabled many workers to propose theories regarding the relations between the colour and the constitution of organic compounds. In this way certain groups of atoms in the complex molecule are recognised as the seat of colour, while the others are supposed to help the formation of colour. These theories interesting and instructive as they are, have met with little success, as they give no quantitative information as to the position and intensity of an absorption band in a given compound, nor any insight into the mechanism by which the light energy is absorbed in a molecule.

Baly<sup>1</sup> and later Henri<sup>2</sup> and others proposed a theory of a semi-quantitative nature regarding the position of the absorption bands in the ultra violet region. According to these authors the position of an ultra violet absorption band is mainly governed by one of the fundamental vibration frequencies of the molecule in the infra-red region of the spectrum. The infra-red frequency when multiplied by a suitable whole number gives the exact position of the absorbed ultra violet frequency. The idea underlying this relation is that the molecule absorbs a definite number of quanta of lower energy which appears later on in the ultra violet as one whole larger quantum. No fixed rule is given regarding the selection of the particular infra-red frequency and obviously, the one suited for the purpose is chosen. Moreover, it is now well recognised, that the ultra violet or the visible, absorption is



influenced by the energy of the outer electrons in a molecular system, while the inner vibrations of the kernels or the nuclei which have considerably lower energy, are mainly responsible for the absorption in the near infra-red. No definite relation between these two energies, electronic and vibrational in a given molecular state, is yet known. However, it may be noted, that some diatomic molecules of which the electronic and vibrational frequencies in a given state are definitely known from the recent data on the band spectra, do show simple relations which may not be merely a matter of coincidence. In Table 1, the electronic ( $\nu$ ) and the vibrational ( $\nu_v$ ) ground frequencies for some of the excited states of the CO molecule are given. It will be seen that the former is a whole multiple ( $n$ ) of the latter, and the deviation from the observed value of  $\nu_e$  is only about 0.5 per cent. Other instances of a similar type can be quoted.

TABLE 1.

$\nu_v^s$	$n$	$n \times \nu$ calc.	$\nu_e^s$ obs
1914	52	99528	99730
2081.5	42	87423	86892
1497.63	43	64398	64729
1105	58	64090	64060
1173	49	57477	57763
1726.5	28	48342	48530

Any approach to the subject of the light absorption in polyatomic molecules must be made with caution. Before we can give a complete explanation of the absorption by a molecule in the free gaseous state, ideas regarding the absorption by solutions or even by liquid substances are likely to be in error. As yet the mechanism of light absorption, in the infra red and the visible or the ultra violet, is understood to a fair degree of accuracy, only in the case of simple diatomic molecules in their stable or metastable forms. The best we can do therefore, for the polyatomic molecules, is to proceed from the analogies offered by the diatomic molecules, and utilise such of the data as are available from the band absorption of such molecules.

The analysis of the absorption band spectrum of a diatomic molecule gives the energy value of the outer electrons, as also the values of the nuclear energy of vibration in the ground and the various excited states. The ground vibrational frequency thus obtained in the lowest energy state of the molecule should then be comparable with its fundamental frequency in the infra-red. In Table II, the third column shows the value of the absorbed infra-red frequency, as measured directly or

as obtained from the data on the Raman effect. The fourth column shows the same value as found from the band spectra.

TABLE II.  
Vibration frequency in diatomic molecules.

Molecule	Bond	$\nu_v$ (i. r.)	$\nu_v$ (band sp.)	Molecule	Bond	$\nu_v$ (i. r.)	$\nu_v$ (band sp.)
H <sub>2</sub>	H-H	4155	4264	HCl	H-Cl	2780	2840
N <sub>2</sub>	N=N	2329	2345	HBr	H-Br	2479	2603
O <sub>2</sub>	O=O	1552	1565	HI	H-I	2233	—
P <sub>2</sub>	P=P	468	450	CO	C-O	2155	2149
S <sub>2</sub>	S=S	470	426	NO	N-O	1877	1892
Cl <sub>2</sub>	Cl-Cl	556	561				

The fair amount of agreement observed in Table II, between the values of vibration frequencies as obtained by the two independent methods, leads us further to examine the question of polyatomic molecules.

A characteristic feature of the polyatomic molecules as revealed by the Raman effect, is that the vibration frequency of any of the individual atomic linkages in them remains constant within narrow limits, whatever the general structure of the molecule. Thus such groups as C-H, C=O, C=C, C=N etc. have definite frequencies which are always found in the molecules containing them. Furthermore, it is interesting to note that these atomic linkages when present in the free diatomic states again exhibit the very same frequencies in their ground vibrational states. Table III shows a comparison of the vibration frequencies of some of the diatomic groups, in the combined and in the free state.

TABLE III.  
Vibration frequencies in diatomic groups.

Molecule	Bond	$\nu_v$ Raman	$\nu_v$ band sp.	Molecule	Bond	$\nu_v$ Raman	$\nu_v$ band sp.
CH <sub>4</sub>	C-H	2910	2815	BiCl <sub>3</sub>	Bi-Cl	240,288	218*307
C <sub>2</sub> H <sub>4</sub>	C=C	1630	1630	SnCl <sub>4</sub>	Sn-Cl	367,401	350,431*
Carbonyl	C=O	1722	1724*	O <sub>2</sub>	Si-O	802,1227	844*1236
Nitrile	C=N	2172	2144*	Sulphate	S=O	617,1107	609*1124
N <sub>2</sub> O	N=O	2223	2345*	Chromate	Cr=O	787,870	746*897
NO	N=O	1877	1892	Vanadate	V=O	870	865*1098
Nitrate	N=O	1047	1030*	Manganate	Mn=O	788,833	758*898

According to this table we recognise for the first time that the individuality of a diatomic group, as regards its characteristic vibration frequency is always preserved, either in the free state or while forming the part of a molecule. This is, however, not the case with the electronic frequency, for the electronic energy of a diatomic molecule would suffer much change while forming the part of a polyatomic molecule. Here, on account of the neighbouring linkages and the heavier mass of the system as a whole, the electronic energy would be considerably damped, with the result that the absorption wave lengths in the visible or the ultraviolet are shifted towards the red side of the spectrum, the amount of shift varying with the degree of damping. The decrease in the electronic energy of the diatomic system would also lower the number of possible vibrational transitions between the two electronic states, and, therefore, the region of absorption now covered by the polyatomic molecule is shorter than before

In order to test the correctness of the views given above, we have to look for the actual band spectra of a large number of molecules in absorption. It is found, however, that only a few of these have been investigated so far, mainly because their analysis is rendered difficult on account of their complexity. The main vibration frequency in each of them however is easily found from the separation of the principal band heads. This would give us the frequency of that part of the molecule which causes in general the absorption of light, and thus we should identify the absorbing group by comparing the principal vibration frequency of the molecule with that of the absorbing group in the diatomic state. In the following table, the principal vibration frequencies, together with the frequencies of the active group in the free state, for some of the molecules are given (Table IV)

The results shown in the above table confirm the views outlined before. It is also found that in the instances cited above, the original band system of the active group is displaced towards the red end, and the region covered in absorption is also much smaller. Further it will be seen that the active group is more unsaturated in character, relative to the rest of the molecule. It may be concluded therefore, that in organic molecules such groups as  $C=O$ ,  $C=C$ ,  $C=N$ ,  $N=N$  and others form the main seat of absorption

Some of the vibration frequencies as observed in the band spectra are marked with an asterisk in table III and IV. These represent the vibration frequency of the diatomic molecule in one of the observed excited molecular state. When this same frequency occurs in absorption in a polyatomic molecule, it probably means that the diatomic group in question is in an excited state, and imparts to the molecule its observed chemical activities. It would be possible to clarify this point, if we could observe any change in the vibration frequency

TABLE IV.  
Principal vibration frequencies in polyatomic molecules.

Molecule	Active group	Polyatomic Frequency	Frequency in Diatomic State.	
Formaldehyde <sup>6</sup>	C = O	1120	1182*	Hopfield Birge upper level.
	C = O <sup>6</sup>	1723	1724*	Cameron upper level.
Phosgene <sup>7</sup>	C = O	422	2149~1724*	Cameron system.
Benzoquinone <sup>8</sup>	C = O	1110	1105*	Merton-Johnson upper level.
			1182*	Hopfield Birge upper level
Diacetyl <sup>9</sup>	C = O	422	2149~1724*	Cameron system.
	C = O	1411	1497*	4th. positive upper level.
Glyoxal <sup>8</sup>	.. C = O	1418	1497*	4th. positive upper level.
Hydrazine <sup>9</sup>	... N = N	470		...
Azobenzene <sup>10</sup>	. N = N	652	2345~1679*	Birge Hopfield abs-system

of the molecule by suitable electronic excitation. This excitation could be brought about by the absorption of light in the visible or the ultra violet. If then, for such a molecule, Raman photographs are secured, while the same is exposed to the ultra violet light, the scattered radiations on the spectrograms would be different from those observed ordinarily:  $\epsilon$  when the exciting ultra violet light is absent. Such experiments would be possible only where the absorbed radiations do not bring about any immediate chemical change in the system, or cause fluorescence in the molecule. Some of the results of Ghosh<sup>11</sup> may be cited to support this argument. These are shown in table V. The frequency shifts which are common to the ordinary visible excitation, as well as to the ultra violet excitation, are omitted from the table. Those of the frequencies which are present exclusively under the ultra violet excitation are shown in the second column, while the third column shows the frequencies which are observed ordinarily in glass apparatus which cuts off most of the ultra violet light, and which are totally absent when quartz apparatus transmitting all the radiations is used. This difference in the two cases is not due to any failure to observe some of the faint lines in the spectrograms. For example, if this were so there is no reason why such a strong line due to the frequency shift 426 in the case of ethyl alcohol should be totally absent when the same substance is under the influence of the ultra violet radiations. There is no doubt that in the latter case we are

dealing with a molecule which has changed its vibration frequency due to a change in the molecular energy level, under the influence of absorbed radiations. However, in order to draw any conclusion as to the energy level reached by a molecule as a result of light absorption we need much more data, obtained from an examination under strictly controlled conditions, of a large number of substances.

TABLE V.  
Raman frequencies in excited molecules.

Molecule	Ultraviolet excitation	Visible excitation.
Methyl alcohol		no difference
Ethyl alcohol	506,2741	426, 1094, 1273
Acetic acid	288, 376, 1002, 1276	440
Ethyl formate	609, 1013	2878
Ethyl acetate	...	938, 1005, 1044
Sodium acetate	...	647, 1649
Ethyl malonate	...	2875.

From what has been said above, it would be sufficiently clear that the whole question of the absorption of light in polyatomic molecules needs a re-examination in the light of the new knowledge gained from the band spectra and the Raman effect. While the existing data on the solutions are useful for their practical applications, in order to understand anything regarding the mechanism of light absorption, we need more quantitative experiments, probably along the lines suggested in this paper.

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## THE BLEACHING OF SHELLAC

By

N. NARNSIMHA MURTY

Shellac is not a single chemical compound but consists of a mixture of several resin acids, wax and a colouring matter called erythrolaccin. The bleaching of such a complex material is a delicate operation especially as shellac is prone to become insoluble on continued heating or in contact with hydrochloric acid, or become hydrolysed to a sticky resinous mass on contact with caustic alkali. A physical method of obtaining a pale resin would be to extract the colouring matter, erythrolaccin with ether leaving behind about 70% of the original shellac which from alcohol solutions gives a colourless film. But such a film is brittle and lacks adhesion as the ether extracts, besides the colouring matter, the resin acids which impart to shellac its unique property of good adhesion and toughness combined with hardness.

The colouring matter could be removed as described by Wolff (1) by filtering the alcoholic solution of shellac through animal charcoal. But the bleaching is incomplete and uneconomical.

According to a method by Dutt (2) the ethyl alcohol solution of shellac is neutralized by ammonia, ethyl amine, or calcium oxide and agitated with Indian bauxite, and filtered.

According to Daum (3) the colouring matter is first taken up by fat (e. g. by treating shellac with a hot aqueous solution of cocoanut oil) and the fat with the colouring matter is then extracted with petroleum ether.

Among the chemical methods of bleaching may be mentioned several processes which involve the oxidation of the colouring matter. By leaving shellac in contact with hydrogen peroxide for several days a light coloured resin can be obtained. The bleaching is, however, incomplete and costly. Hydrogen peroxide does not bleach alkaline solutions of shellac. According to Venugopalan (4) reducing agents like sulphurous acid give a green coloured product, the decolorization being incomplete. Treatment of shellac with drastic oxidizing agents like nitric acid leaves behind a yellow sticky mass, the rupture of the heavy molecules of resin acids taking place at the double bond and hydroxyl groups.

The most common bleaching agent is chlorine. On account of its great activity and the possibility of rendering shellac insoluble

direct chlorination of shellac is not feasible. But this can be accomplished according to the method of Gratzel (5) by leading into the alkaline solution of shellac chlorine which has been diluted with a large quantity of air or other inactive gases. It is more convenient, however, to add chlorine in the form of sodium hypochlorite. According to the method of Rosenhagen (6) the production of sodium hypochlorite from sodium chloride and bleaching of shellac is carried out electrolytically in one operation.

Sodium hypochlorite should be prepared fresh every time before bleaching, the method described by Zoller (7) being most convenient. Bleaching is best carried out between  $30^{\circ}$  to  $34^{\circ}\text{C}$ .

The chief factor that enters into the economy of bleaching shellac on a commercial scale, especially in India, is the cost of sodium hypochlorite. Hence professional bleachers should select low hypochlorite consuming shellacs consistent with price. Shellac in general consumes less hypochlorite than seed lac, being comparatively free from the dye laccic acid and nitrogenous matter. But there is a tendency among bleachers now-a-days to use more and more seed lac for bleaching, partly on account of its cheaper price and partly because the wax can be easily filtered out of the hot alkaline solution, whereas, with shellac, the wax is in a more stable suspension owing to the previous heat treatment it has undergone, and filtration is difficult. Addition of a small quantity of kieselguhr to the solution and stirring makes the removal of wax easier.

Seed lac contains in varying amounts lac dye, insect scarf, and woody material as impurities, and these are chiefly responsible for the increased consumption of the bleaching agent. One gramme of water extractable material consisting of laccic acid, sugars, and proteins is present on an average in every 20 gm. of stick lac, and one gramme of this extracted material requires for bleaching its alkaline solution to a yellow colour 42 c.c. of a solution of hypochlorite (containing 3% available chlorine), whereas 20 gm. of a well washed Khair seed lac takes only 30 c.c. of the same hypochlorite solution for bleaching its alkaline solution to a light wine colour.

More than the dye the albuminous matter and the ammonia salts present in seed lac are responsible for the excess of sodium hypochlorite consumed. This is evident from the following experiment. 15 gm. of a sample of shellac required 28 c.c. of sodium hypochlorite (having 3% available chlorine) for bleaching its alkaline solution to a light wine colour. But when its nitrogen content was raised by half per cent. by addition of ammonium sulphate to the alkaline solution it required 62 c.c. of the same bleaching solution. When its nitrogen content was raised by one per cent. it required 91 c.c. of the hypochlorite; the

bleaching was still unsatisfactory and the colour tended to return on keeping the solution.

The dye and the albuminous matter can, however, be easily washed out if the freshly cut lac is immediately washed, as then the dye and the albuminous matter will be in a soft condition. But with stick lacs stored for a long time the dye and the albuminous matter will have hardened and it will be difficult to wash away these from the interstices of the lac grains. The water used in washing must not be hard, otherwise, the removal of the dye from the seed lac will be incomplete due to the precipitation of calcium salt of laccaic acid in the interstices of the lac grain.

Washing with Fuller's earth, or with weak alkalies such as sodium carbonate or borax will be useful. The greater the concentration of sodium carbonate the easier it is to remove the dye, but, at the same time, loss is encountered on account of a portion of the lac also getting into solution and being washed away. Hence a compromise has to be effected. The advantage of washing with sodium carbonate will be clear from the following experiment. A sample of 'punk' stick lac gave on machine washing with tap water a 68% yield of seed lac. 20 gm of this seed lac required 82 c.c. of sodium hypochlorite solution (containing 3% available chlorine) for bleaching its alkaline solution. Further mechanical washing of this seed lac with 0.025% sodium carbonate solution resulted in a loss of 2% of seed lac. But 20 gm. of this seed lac now required only 70 c.c. of the hypochlorite solution. The concentration of the sodium carbonate solution could be increased up to 0.1% with beneficial results.

In dealing with shellac we have to deal with different impurities, namely resin and orpiment. Resin is present in most TN samples being added during its manufacture in order to help the melting of difficultly fusible lacs. It has no adverse effect on bleaching. Orpiment on the other hand which is added to lighten the colour of TN shellacs has a marked effect in increasing the quantity of bleach required. So long as appearance remains one of the chief criterions in the purchase of shellac orpiment will continue to be an ingredient of TN grades. It is desirable to know, however, to what extent its presence can be tolerated in bleaching.

To obtain definite information on this subject it is necessary to compare samples made from the same seed lac with and without orpiment. This is of extreme importance as some dark coloured samples require more than twice the quantity of bleach that is required for light coloured ones. Seed lacs ranging from fairly light colour to dark colour were taken and various amounts of orpiment incorporated. 10 gm. of the above powdered samples were dissolved in 100 c.c. of sodium carbonate solutions of various strengths at 60°-65°C on a



water bath for 2 to 3 hours and the solution then decanted. Sodium hypochlorite solution whose available chlorine had been previously determined and adjusted to contain 4.7% available chlorine was added in lots of 3 c.c. in the beginning and in fractions of one c.c. towards the end of bleaching, (the next lot being always added after ensuring the absence of free chlorine with the help of starch-iodide paper). The results are incorporated in Table 1.

TABLE I.

Sample No.	Orpiment content % 1	c.c. of bleach required in solution of		
		1% $\text{Na}_2\text{CO}_3$ 2	2% $\text{Na}_2\text{CO}_3$ 3	5% $\text{Na}_2\text{CO}_3$ 4
1 (control)	nil	11.8	14.0	14.5
2	1.2	12.1	17.0	18.5
3	2.3	12.6	21.5	.
4 (control)	nil	10.0	..	...
5	0.13	10.5	..	...
6	0.25	10.5		.
7 (control)	nil	.	12.0	...
8	0.08		12.2	...
9	0.15	...	12.3	...
10	0.30	.	13.4	...

It will be evident from the table that with increasing quantity of orpiment the amount of bleach required increases. With small quantities of orpiment, i.e. below 0.3%, the difference is small. When the concentration of alkali is increased, however, the difference becomes marked (vertical columns 3 and 4 in Table I). This is to be expected as with increasing concentration of alkali more orpiment goes into solution. It was also noticed that when the alkaline solutions were treated with excess of hypochlorite the controls took the least time to attain the light colour while the others took longer periods in order of their orpiment content.

The fact that orpiment uses up a portion of the hypochlorite is established thus. A sodium carbonate solution of 0.1 gm. of precipitated orpiment ( $\text{As}_2\text{S}_3$ ) is left in contact with a known excess of standard sodium hypochlorite solution for 72 hours, the unused available chlorine being determined at the end of that period. It is found

by this method that 5.3 c.c. of sodium hypochlorite solution (having 4.76% available chlorine) is taken up by 0.1 gm. of orpiment.

The concentration of sodium carbonate solution itself influences the amount of sodium hypochlorite consumed even when orpiment is absent. This is clear from Table II. Vertical columns 2 and 3 represent in c.c. the amount of bleach (having 5% available chlorine) required for 10 gm. of shellac.

TABLE II.

1 Concentration of $\text{Na}_2\text{CO}_3$	2 Shellac (light coloured)	3 Shellac (dark coloured)
1%	11.0	5.5
2%	11.5	5.9
5%	13.5	6.5

Increase of alkalinity often results in the precipitation of a gelatinous mass of shellac. Another danger of higher concentration of alkali is the hydrolysis that will be brought about while dissolving. It is therefore preferable to dissolve shellac in a carbonate solution less than 2% strong. Some old lacs take longer time to dissolve in this concentration, preliminary swelling taking place before dissolving.

When the bleaching operation involves the use of large quantities of hypochlorite the quality of the resulting bleached lac is generally poor. The colour is dull and the bleached lac soon becomes insoluble.

Apart from the oxidation of the colouring matter during bleaching, chlorine adds itself at the double bond of the resinous constituents of shellac. Hence the iodine value decreases from about 18 in ordinary shellac to about 9 in bleached lac. Addition of a trace of cobalt hydrate is helpful during bleaching, the action of cobalt hydrate on sodium hypochlorite being the liberation of oxygen, which is supposed to direct the process of bleaching chiefly towards one of oxidation. The presence of sodium silicate is also supposed to increase the efficiency of sodium hypochlorite.

After completion of bleaching, the alkaline solution may be partially neutralized and concentrated, and this solution can be used as such for playing cards, for stiffening felt hats, and as gloy substitute. For obtaining the solid resin the alkali is neutralized with hydrochloric acid (dilute), dilute sulphuric acid, or acetic acid. The first one gives a more granular precipitate of bleached lac, while acetic acid gives a product which has less tendency to become unfusible. In order to mitigate the harmful effect of any free chlorine present the alkaline

solution is treated with sodium sulphite before the precipitation, or, as recommended by Watson and Mulany (8), the granular precipitate of bleached lac is treated with sodium thiosulphate solution before washing. The last traces of electrolyte which are ordinarily difficult to remove by washing can be removed from bleached lac by electro-dialysis. The resulting bleached lac can be stored in the form of dry powder (vacuum dried containing about 6% moisture), or under water, or in the form of spirit varnish. When stored under water bleached lac retains its solubility for a longer time because the hydrochloric acid formed from the chlorine present in bleached lac gets diluted by the water. Spirit solutions of bleached lac become nondrying when preserved for a long time. The chlorine present in bleached lac forms hydrochloric acid in presence of moisture which acts as a catalyst bringing about the esterification of bleached lac with alcohol. The ester being like molasses in consistency renders the film tacky. Owing to these defects too much time should not be allowed to lapse between production and consumption of bleached lac.

#### ACKNOWLEDGMENT.

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# LIFE AND WORK OF SIR P. C. RAY, Kt., C.I.E.,

PH. D., D. Sc.

By

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A brilliant chemist, Professor Sir P. C. Ray, is aptly known as the Father of Chemical Research in India. Not only he has been himself enthusiastically engaging his attention in the pursuit of Chemistry but he has always been ready to sacrifice his all for inspiring the love for research among students who were fortunate to sit at his feet.

The Indian Chemical Society has recently published a Jubilee Volume to commemorate the valuable services rendered by Sir P. C. Ray to the cause of science. The publication, in this volume of the Bombay University Journal, of the following short account of Prof. Ray's life and the scientific work done by him will be a fitting appreciation of his achievements.

Prafulla Chandra was born on 2nd August, 1861 in a small village in Khulna District in Bengal. His father was a very enlightened person and took keen interest in education. He himself was a good scholar of Persian and also knew a little bit of Arabic and Sanskrit. Being a person of advanced views he felt the need of educating the boys and girls of his village and to that end he started the first Girl's School and a Middle English School, mostly at his own expense.

Prafulla Chandra and his two elder brothers were given their early education at their father's school which is still in existence. To enable his elder brother who had passed the minor scholarship examination, to prosecute his studies further the family moved to Calcutta in August, 1870. Prafulla Chandra was admitted into the Hare School where he had a very distinguished career. But in August, 1874 he got a severe attack of dysentery and had to give up his studies for two years. While a student of the Hare School and during his illness Prafulla Chandra read the works of several English writers and contracted a liking for English literature. At about the same time he was struck with the close similarity of Latin to Sanskrit and lost no time in learning up the new language.

After his recovery—the attack of dysentery having left him a permanent valetudinarian—he took admission into the Albert School where he was much liked by his class teachers and his liking for the English

literature grew into love because of the excellent method of teaching of Krishna Behary Sen, the rector of the school.

After passing the Entrance Examination Prafulla Chandra joined the Metropolitan Institution particularly with a view to receive instructions in English literature, prose and poetry, from Sir Surendranath Banerjee and Prasanna Kumar Lahiri who were distinguished teachers of the subject. While a student of the Institution he was also attending the lectures in Physics and Chemistry at the Presidency College, Calcutta, as an external student. It was at this time that the seeds for a rich harvest were sown. Prafulla Chandra was very much influenced by the lectures and the experimental skill of Prof. Sir Alexander Pedler and began to acquire a taste for chemistry. He soon saw that the future progress of India depended upon the advancement of scientific education.

At about the same time Prafulla Chandra appeared privately for the Gulchrist Scholarship examination and was one of the two Indian winners. This gave him an opportunity to go to Europe to prosecute his further studies in chemistry. His parents did not object to his going out of India and he proceeded to England with the idea of joining the University of Edinburgh which was in those days considered to be a seat of learning. He received his lessons in chemistry from Professor Alexander Crum Brown under whom he afterwards worked for the degree of Doctorate of Science. He took the B.Sc. degree in 1885 and D.Sc. in 1887 on the submission of a thesis. Some of this work has been published in Dr. Ray's first paper on 'Mixed double sulphates of copper and magnesium group' in the proceedings of the Royal Society of Edinburgh.

Dr. Ray was the recipient of the Hope Prize Scholarship in chemistry during 1887-88 and this gave him an opportunity of assisting Professor Brown and Dr. Gibson in the laboratory teaching. The same year he was elected as the Vice-President of the Edinburgh Chemical Society. Professor Sir James Walker who has lately retired from the chair of Physical Chemistry at the Edinburgh University and Professor Hugh Marshall, the discoverer of persulphuric acid, were his colleagues at the chemical laboratory.

In 1888, Dr. Ray returned to India. A year after, he was appointed as an assistant professor of chemistry at the Presidency College, Calcutta, where he ultimately succeeded Professor Pedler. Soon after his appointment he started research work on various problems but it was in 1896 that Dr. Ray made his celebrated discovery of mercurous nitrite. He found that when dilute nitric acid is placed in contact with mercury at about  $30^{\circ}$ , fine yellow needles of mercurous nitrite are deposited on the surface of mercury. Thus he was the first not only to indicate the mode of formation but also to isolate the mercurous

salt which was then unknown to the chemical world. The results of this remarkable discovery were published the same year in the *Journal of the Asiatic Society, Bengal*, *Zeitschrift für Anorganische Chemie* and in the *Proceedings of the Chemical Society, London*, and Dr. Ray entered upon a new era of his scientific career. He then proceeded to study the chemical behaviour of mercurous nitrite and found that it slowly dissolves in the mother liquor forming (i)  $\text{Hg}_2(\text{NO}_2)_2$  and (ii) a basic nitrate. When a solution of mercurous nitrite is spontaneously evaporated (i)  $\text{Hg}_2(\text{NO}_2)_2$ ,  $2\text{H}_2\text{O}$ , (ii) two basic mercurioso-mercuric nitrites and (iii) a basic mercuric-nitrite are formed. When mercurous nitrite is dissolved in water 78% of it gets dissociated into mercurous mercury and mercuric nitrate, the limit to dissociation being caused by the formation of a stable compound mercurioso-mercuric nitrite.

While attempting to elucidate the mechanism of the formation of mercurous nitrite Dr. Ray took no time in finding that the presence of nitrous acid is essential for the dissolution of mercury into nitric acid. In the early stages of the reaction nitric acid and nitrous acid, which is always present in nitric acid in small amounts, both react with mercury as



Later on the nitric acid reacts with mercuric nitrite yielding mercurous nitrate and nitrous acid. After some time the quantity of nitrous acid reaches a constant value and it then begins to act as a catalytic agent between nitric acid and mercury. The third stage of the reaction is then represented by



The rate of this reaction of mercury with nitric acid was found by him to be influenced appreciably by the presence of other substances: it was retarded by ferrous and ferric salts and accelerated by the salts of sodium and manganese.

When mercurous nitrite is heated it decomposes into mercurous nitrate and nitric oxide mixed with very little nitrogen peroxide and there also appear small quantities of metallic mercury, orange coloured mercury oxide and a basic nitrate. In order to explain the formation of the products of decomposition Dr. Ray assigned the oxylic,  $\text{HgO} \cdot \text{NO}$ , and the non-oxylic,  $\text{Hg} \cdot \text{NO}_2$ , formulae to mercurous nitrite and substantiated them by the reaction of ethyl iodide with mercurous nitrite in which both ethyl nitrite and nitro-ethane are obtained.

Encouraged by these successes Dr. Ray opened up new avenues of research. From mercurous nitrite to mercuric and mercurous hyponitrites was the next step. With this end in view he treated a solution of mercurous nitrite with the sodium hyponitrite but found that a mixture of mercuric and mercurous hyponitrites is formed. The

separation of the two hyponitrites was not difficult for him. He soon found that if the solution of mercurous nitrite is first treated with sodium chloride and filtered and sodium hyponitrite is then added to the filtrate a fairly pure sample of mercuric hyponitrite is obtained. However, Dr. Ray found later that a pure sample of mercuric hyponitrite could be readily prepared by the action of a concentrated solution of potassium cyanide on mercuric nitrite.

A pure sample of mercurous hyponitrite was obtained by precipitating (i) mercurous-mercuric nitrite with crude alkaline hyponitrite and (ii) mercurous nitrate with carefully neutralised sodium hyponitrite. The mercurous hyponitrite dissolves in dilute nitric acid but the solution becomes opalescent on standing due to its dissociation into mercury and mercuric nitrite. On heating, mercurous hyponitrite decomposes. The main products of decomposition are mercury, mercuric oxide and oxides of nitrogen with small quantities of mercurous nitrite and nitrogen. This led Dr. Ray to conclude that while being heated only half of the mercurous hypo-nitrite exists in the oxylic form  $\text{Hg N O}$ , while the other half assumes the imidic structure  $\text{Hg O. N. N. O. Hg}$ .

When the filtrate obtained after the treatment of a solution of mercurous nitrite with sodium chloride was treated with excess of ammonia, a white precipitate of a new salt, dimercuriammonium nitrate,  $2\text{NHg}_2\text{NO}_2 \cdot \text{H}_2\text{O}$ , was obtained. This opened up a new field for investigation and subsequently resulted in the preparation of a series of compounds known as dimercuriammonium compounds. On treating a solution of dimercuriammonium nitrite with  $\text{HCl}$  and  $\text{HBr}$ , Dr. Ray obtained another series of salts, mercuriammonium chloride and bromide the latter on treatment with  $\text{KOH}$  gave dimercuriammonium chloride and bromide. But the action of nitric acid on  $\text{NHg}_2\text{NO}_2 \cdot \frac{1}{2}\text{H}_2\text{O}$  directly gave dimercuriammonium nitrate identical with the compound obtained by the action of ammonia on mercuric nitrate.

Dr. Ray's work was now getting recognition. In order that Dr. Ray may come into touch with up-to-date methods of research the Government of Bengal deputed him, in 1904, to visit the chemical laboratories in Europe. During his short stay, he himself worked on the dimercuriammonium compounds at the Davy-Faraday laboratory and met a number of distinguished chemists in England and on the continent, chiefly Sir William Ramsay, James Dewar, Emil Fisher, van't Hoff and Berthelot who were pleased to take him round their laboratories and to explain to him the important work done by them.

On his return Dr. Ray started his investigation with redoubled vigour. Because of its instability, all attempts to obtain mercuric nitrite in the solid state had hitherto resulted in failure. Dr. Ray set himself to work on the preparation of this unstable compound and

found that if equimolecular quantities of pure silver nitrite and mercuric chloride are rubbed together to a fine paste with water, a yellow solution is obtained and this on concentrating under vacuum over sulphuric acid yields tufts of fine needles of  $\text{Hg}(\text{NO}_2)_2$ . When the needles are exposed to air, they readily decompose but they could be kept as such indefinitely in completely evacuated sealed tubes. Dr. Ray had thus discovered a new technique for the preparation of mercuric nitrite and was naturally led to the preparation of such other nitrites which easily decompose on exposure to air. He, however, boiled the mixture of silver nitrite and the chloride of the base in the case of fairly stable nitrites. He thus prepared nitrites of the alkali metals and of metals of the alkaline earth, but later on he found it more convenient to use barium nitrite and the sulphate of the base for the preparation of the nitrites of other metals. In the same way by using silver nitrite and the hydrochloride of a number of alkyl, iso-alkyl, aryl and alkyl-aryl amines he succeeded in preparing their ammonium nitrites. But when he attempted to prepare these nitrites by using mercuric nitrite and alkyl and aryl amines, he not only obtained the alkyl and aryl ammonium nitrites but also a series of mercuri-alkyl and mercuri-alkyl-aryl ammonium nitrites.

Having obtained the various nitrites by the method of causing the substances to react by rubbing them together into paste with water, Dr. Ray extended the use of this method to the preparation of double nitrites of mercury with those of other metals. He thus obtained a series of mercuric alkali-metal and mercuric alkaline earth metal nitrites. Further he showed that these nitrites and the mercuri-alkyl and mercuri-aryl ammonium nitrites are complex and not the double salts, the mercury forming the complex anion and the alkali metals and metals of the alkaline earth the cation.

An attempt was then made to study some of the physical and chemical properties of these nitrites. He mainly studied their molecular volumes and the action of heat upon them. It was found that all nitrites decompose on heating. The decomposition products of the nitrites of alkali metals and those of alkaline earth were in general, oxides of nitrogen and a basic nitrate which on further heating broke up into oxygen and the oxide of the metal. But the alkyl and the aryl ammonium nitrites did not show any regularity in their behaviour on heating. In general they decomposed into nitrogen or oxides of nitrogen and some other alkyl and aryl compound depending upon the nature of the alkyl and the aryl group in a particular nitrite. Whilst Ray was in the midst of discovering new series of compounds he was called away from his work and had to proceed to Europe for the third time to represent the Calcutta University at the Congress of the



Universities of the Empire in 1912 at London. He made the best use of this opportunity by reading a paper on the vapour density of ammonium nitrite before the Chemical Society. Dr. Ray had previously discovered that contrary to text-book statements, ammonium nitrite could be obtained in a stable crystallized condition. When an aqueous solution of the salt is heated at  $37-40^{\circ}$  in vacuum only a small amount is decomposed and at  $70^{\circ}$  most of it sublimes unchanged. It created a mild sensation amongst the chemists when Dr. Ray presented the vapour density data, obtained with the assistance of Dr. N. R. Dhar, which showed that ammonium nitrite unlike ammonium chloride does not undergo dissociation.

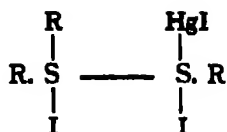
While in England, he received an invitation from Sir Asutosh Mukherjee, the Vice-Chancellor of the Calcutta University, to occupy the newly founded chair of chemistry at the University College of Science, Calcutta. He gladly accepted the offer and retired from the Presidency College in 1916 to take up the newly created Palit Professorship in Chemistry—the chair which he holds uptill to-day.

Dr. Ray's later work, carried during the years 1912–1916 at the Presidency College and from 1916 onwards at the laboratories of the Science college, forms a very important contribution to synthetic chemistry and the varying valency of certain metals. The method of preparing nitrites described in the previous pages was extended to the case of several other metals and cadmium, zinc and gadolinium nitrites were obtained. Also a series of alkaloidal derivatives of mercuric nitrite was prepared and the electrical conductivity measurements of aqueous solutions of some of them confirmed the previous conclusions that these are complex and not the double compounds. In a similar way a series of mercuri-alkyl and mercuri-alkylaryl-ammonium chlorides was obtained

When mercuric nitrite was treated with mercaptans, nitromercaptan  $R\ S\ HgNO_2$ , and compounds of the type  $R\ S.HgNO_2.Hg(NO_2)_2$  were formed.  $Et\ S.HgNO_2$  with ethyl iodide yields yellow tablets of  $Et_2S_2.HgI_2.EtI$  which has been shown to be a sulphonium derivative,  $SRR'I$ .  $SRI$ ,  $HgI$ .

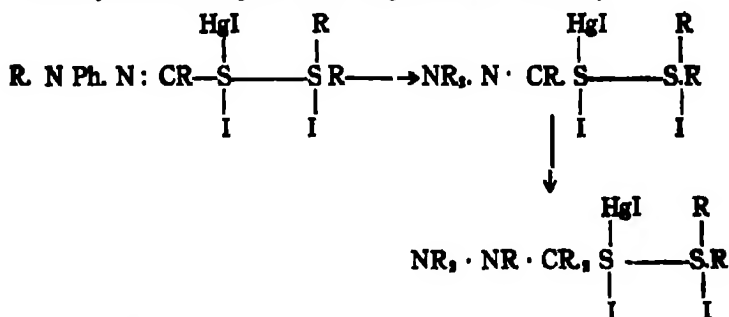
When mercury mercaptide nitrite was similarly treated with butyl iodide it was found that one of the methyl groups is replaced by the butyl, yielding  $MeS_2.C_4H_9.HgI_2.C_4H_9I$ . It was observed that, in general, the lighter radicals are invariably displaced by heavier ones. Later experiments, however, showed that the ethyl group could be replaced by methyl provided the methyl iodide is taken in large excess, the displacement of one group by another being governed by the Law of Mass Action.

Only two atoms of iodine of the sulphonium compound were found to be replaceable when its aqueous solution was treated with  $AgNO_3$ , for, as will be seen from the general formula,

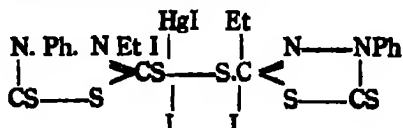


the third atom of iodine forms a part of the complex radical (HgI). However in acetone solutions, Dr. Ray found that all the three atoms of iodine are precipitated quantitatively by  $\text{AgNO}_3$ . He thus discovered a method of preparing a series of disulphonium compounds in which all the atoms of iodine are replaced by other acid radicals on treating the disulphonium iodide by an acetone solution of the silver salt of the radical.

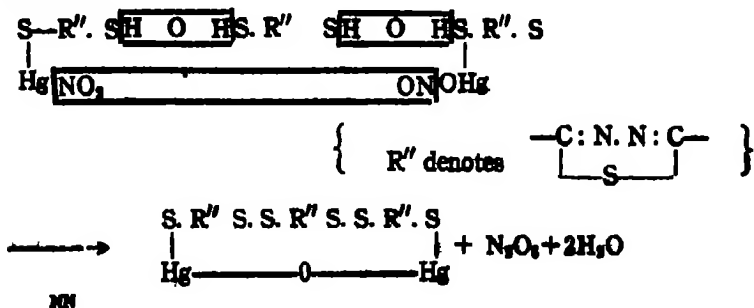
When 2-thio-3 phenyl-2, 3 dihydro-1, 3; 4 thiodiazole disulphide was treated with  $\text{HgNO}_3$  and the resulting product allowed to react with alkyl iodide an open chain compound was obtained.



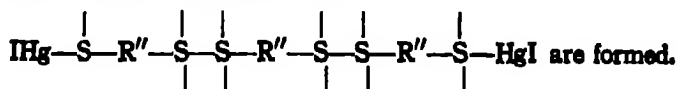
But if the reaction with ethyl iodide is carried out in carbon disulphide solution a ring compound is obtained,



When the dimercaptans of which 2:5-dithiol-1:3:4-thiadiazole is a typical example, are similarly treated with  $\text{HgNO}_2$ , the nitrous acid disengaged in the reaction, oxidises the hydrogen atoms of two or more molecules



and yields a closed chain sulphony compound. Alkyl iodides rupture the ring and compounds of the type



The K-atom of the potassium salts of the cyclic complex monomercaptides was found by Dr. Ray to be singularly reactive towards halogenated organic compounds. But the potassium salts of the dimercaptides were almost inert because two SK groups of these salts exercise an inhibitory influence. The reactivity is, however, greatly enhanced by the introduction of a negative group like  $(\text{NO}_2)$ . The electrical conductivity data in acetone solutions showed that these disulphonium derivatives behave like true salts.

But while attempting to prepare the sulphonium derivatives of other metals by the method described above, Dr Ray found that instead of  $\text{R}_3\text{S}_2\text{MI}_2$ ,  $\text{R}_3\text{SI}.\text{MI}_2$  and  $2\text{R}_3\text{SI}.\text{MI}_2$  (where  $\text{M} = \text{Cd}$  or  $\text{Zn}$ ) were invariably obtained. By modifying the conditions of the reaction he also succeeded in preparing the corresponding mercury compounds. From a comparison of these two types of compounds with  $\text{KHgI}_2$  and  $\text{K}_2\text{HgI}_4$  the structures  $\text{R}_3\text{SMI}_2$  and  $(\text{R}_3\text{S})_2.\text{MI}_2$  were assigned to them. Antimony halide under similar conditions gave a number of complexes of the type  $\text{SbX}_3.\text{R}_3\text{SX}$  and  $(\text{R}_3\text{S})_2.\text{SbX}_3$  ( $\text{X} = \text{I}, \text{Br}, \text{or Cl}$  and  $\text{R} = \text{alkyl}$ ). On the other hand hydrochlor-auric acid, auric chloride and silver nitrate yielded additive compounds of the type  $\text{AuCl}_3.\text{R}_3\text{S}$ ,  $\text{AuCl}.\text{R}_3\text{S}$ ,  $\text{AgNO}_3.\text{R}_3\text{S}$  and  $\text{AgNO}_2.\text{R}_3\text{S}_2$ .

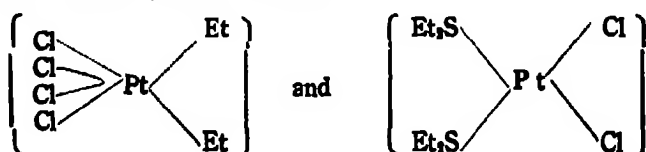
Dr. Ray prepared another series of interesting compounds by passing steam for a very long time over a mixture of ethylene dibromide and potassium hydrogen sulphide. The milky distillate after the removal of alcohol and ethylene mercaptan solidified to a crystalline mass which was found to be triethylene trisulphide  $(\text{C}_2\text{H}_4)_3\text{S}_3$ —this formula being preferred because of the formation of the compound  $(\text{C}_2\text{H}_4)_3\text{S}_3.\text{PtCl}_2$ . The non-volatile oily residue was, on the other hand, found to be a mixture of three polymeric triethylene tetra-sulphides. By the action of mercuric nitrite and mercuric chloride on these sulphides, derivatives of the type  $(\text{C}_2\text{H}_4)_3\text{S}_3.2\text{Hg}(\text{NO}_2)_2$  and  $(\text{C}_2\text{H}_4)_3\text{S}_3.3\text{HgCl}_2$  were obtained. The sulphides and their derivatives, on oxidation with  $\text{KMnO}_4$  or dilute  $\text{HNO}_3$ , yielded various sulphones, sulphinic and sulphonic acid derivatives.

By the interaction of dithioethylene glycol and  $\text{C}_2\text{H}_4\text{Br}$ , 1: 4-dithian was prepared. The polymer of dithian obtained by Victor Meyer was found to be a mixture of brominated long chain compound. The compound,  $\text{Br}.\text{C}_2\text{H}_4(\text{SC}_2\text{H}_4)_n\text{Br}$ , found in the mixture was the first instance of crystalline organic sulphur compound having a very high molecular weight (3068).

In 1915, Dr. Ray had found that with platinic chloride, ethyl mercaptan yields under normal conditions chloroplatinum mercaptide  $(Et_3)_2PtCl$  and under special conditions  $(Et_4S)_2Pt$ . Also dithio-ethylene

glycol yields a chloromercaptide  $C_2H_4 \begin{array}{c} \diagup S \\ \diagdown S \end{array} Pt Cl. S. C_2H_4. SH$ . In

all these compounds he showed that platinum acts as a tri- or divalent element and contrary to the views held by Reynolds, Prätorius-Seidler and Kurnaker, forms a part of the complex radical. On Werner's Co-ordination theory Dr. Ray represented the complexes  $(Et_3S)_2PtCl_4$  and  $(Et_4S)_2PtCl_2$  as

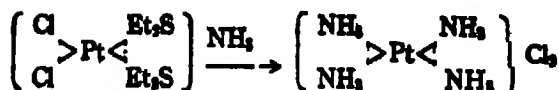


As expected from these constitutions the compounds were found to be non-electrolytes. A direct proof of the variability of valency of platinum was obtained from the study of the reaction between platinic chloride and (i) 2-thiol-5-thio-4-phenyl-4,5-dihydro-1,3,4-thiodiazole



solutions of different concentrations and carrying out the reaction at different temperatures it was found that compounds  $Pt(S. C_2H_4. SH)_x$  where  $x = 3, 4, 5, 6$  or  $8$ , were obtained. At room temperature the hexa-compound was invariably formed, but at lower temperatures, the octa-compound and at higher temperatures, the tri-, tetra- and penta-compounds were obtained. Also when the reaction was conducted at room temperature with a dilute solution, the penta instead of the hexa-compound was formed. Thus Ray concluded that the valency of platinum is a function of temperature and the concentration of the reactants and explained the formation of these compounds on the kinetic theory of molecules.

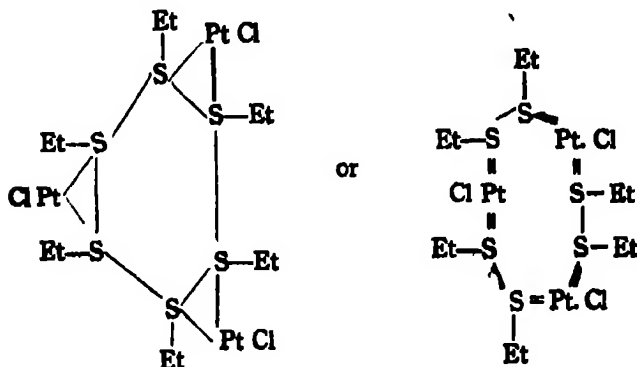
In order to obtain further evidence for the varying valency of platinum Dr. Ray studied the action of ethyl and methyl sulphides on platinic chloride and obtained a series of compounds like  $R_3S.PtCl$ ,  $(R_3S)_2PtCl_2$  (six isomers),  $(R_3S)_3PtCl_3$ ,  $(R_3S)_4PtCl_4$  and  $(R_3S)_5PtCl_5$ ,  $2H_2O$ , some of which were assigned constitutional formulae on Werner's theory. The above complex compounds when treated with ammonia and other organic bases yielded products which throw considerable light on the constitution of the parent bodies. All the six isomers of  $(Et_3S)_2PtCl_2$  gave the same product according to the following:—



The above reaction in which any organic base can be substituted for ammonia, shows that the alkyl sulphide can be exchanged by  $\text{NH}_3$  and the organic base. But in a similar reaction with  $(\text{Et}_2\text{S})_2\text{PtCl}_2$ ,  $\text{PtCl}_2 \cdot 4\text{NH}_3$  was isolated from the reaction product and this indicated that it is not a co-ordination but a molecular compound of the structure  $[(\text{Et}_2\text{S})_2 \text{Pt Cl}_2]_n$ .

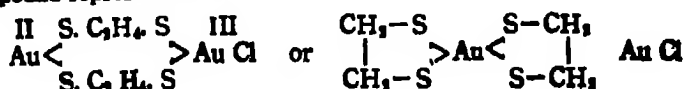
Further, some compounds were prepared by the action of chloro-platinic acid on triethylene trisulphide and benzyl and methyl sulphides. These also confirmed the varying valency of platinum and the constitutions of some of them could be represented on Werner's theory while others were shown, by the reactions indicated above, to be molecular compounds.

In alcoholic solution some of the platinum compounds undergo polymerisation. Thus  $\text{Et}_2\text{S}_2\text{PtCl}$  polymerises into

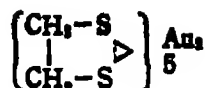


in which case platinum again behaves either as a tri- or penta-valent element.

Gold was also found to exhibit similar variations in valency forming compounds with mercaptans and organic sulphides in which it acts as di-, tri-, tetra- and penta-valent element.  $\text{AuCl}_3$  and  $\text{Et}_2\text{S}_2$  gave a compound  $2\text{AuCl}_3 \cdot \text{Et}_2\text{S}_2$  in which gold is divalent. The same halide reacts with monopotassium salt of dithioethylene glycol yielding a compound represented as



Gold in these compounds behaves as di-, tri- or tetravalent element. If a similar reaction with sodium dithioethylene glycol be carried out in acetone solution, a penta-valent gold compound



is obtained.

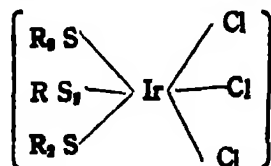
When benzal-diethylene trisulphide was similarly treated, compounds of the type  $6\text{R.Au}_4\text{Cl}_3$ ;  $5\text{R.Au}_3\text{Cl}_3$ ;  $4\text{R.Au}_2\text{Cl}_3$ ;  $4\text{R.Au}_3\text{Cl}_3$ ;  $3\text{R.Au}_3\text{Cl}_3$ ;  $3\text{R.Au}_2\text{Cl}_3$  (where  $\text{R} = \text{S} \left\langle \begin{array}{c} \text{CH}_3 \\ | \\ \text{CH}_3 \end{array} \right\rangle \text{S}$ , 1: 4-dithian) were obtained.

Some of these compounds were shown to be sulphonium derivatives in which Au shows variable valency while others were found to be molecular compounds.

Similarly when iridium tetrachloride was treated with methyl, ethyl and diethyl sulphides it gave the compounds  $\text{IrCl}_4.3\text{Me}_2\text{S}$ ,  $\text{IrCl}_4.2\text{Me}_2\text{S}$ ,  $\text{Ir}_2\text{Cl}_6.4\text{Me}_2\text{S}$ ,  $\text{IrCl}_4.3\text{Et}_2\text{S}$ ,  $\text{Ir}_2\text{Cl}_6.4\text{Et}_2\text{S}$  and  $(\text{IrCl}_2)_3.3\text{Et}_2\text{S}$ . This indicates that iridium like platinum and gold has also a variable valency. Iridium compounds were found by Ray to be much more stable than the corresponding platinum compounds.  $\text{IrCl}_4.2\text{Me}_2\text{S}$  resisted all attempts to split up into  $\text{IrCl}_3.2\text{Me}_2\text{S}$  and  $\text{IrCl}_5.2\text{Me}_2\text{S}$  and was therefore represented as



The compounds  $\text{IrCl}_4.\text{R}_2\text{S}$  which have no platinum analogue ( $\text{R}$  = alkyl group) were on the same grounds assigned the structure



While Dr. Ray was preparing new series of interesting compounds he did not let the work on double salts which formed the starting point of his research career to be at all neglected. He prepared (i) double sulphates of the type  $\text{M}''\text{SO}_4.(\text{R}_2\text{S})_n$ ,  $\text{SO}_4.\text{XH}_2\text{O}$  (where  $\text{M}'' = \text{Zn, Cd, Mg, Mn, Cu, Ni, Co, Fe}$ ), (ii) salts of the type (a)  $\text{X}_2\text{BeF}_4.\text{YSO}_4.6\text{H}_2\text{O}$  which are isomorphous with double sulphates and fluoberyllates and (b)  $\text{MPO}_3.\text{FXH}_2\text{O}$ ;  $\text{MSO}_4.(\text{NH}_4)_2\text{PO}_3\text{F}.6\text{H}_2\text{O}$ ; and  $(\text{NH}_4)_2\text{PO}_3\text{F}.\text{Al}_2(\text{PO}_3\text{F})_3.24\text{H}_2\text{O}$  which are isomorphous with sulphates, double sulphates and alums, respectively. It will be seen that in the (b) class of compounds  $(\text{PO}_3\text{F})$  radical behaves like  $\text{SO}_4$ .

This account of Dr. Ray's activities as an investigator shows what an enormous amount of research work (vide Bibliography at the end) has been published from his laboratory. Most of this work is the outcome of his great discovery of the mercurous and mercuric nitrides

for which Armstrong has rightly given him the name 'Master of Nitrites'. The earlier work was singly carried out by Prof. Ray but much of his later work has appeared jointly with students who from time to time took the degree of the Doctor of Science on the presentation of a thesis and some of them were the recipients of the Blue Ribbon of the Calcutta University—the Premchand Roychand Scholarship. Dr. Ray's first research scholar was Jatindra Nath Sen and prominent, among those who followed are Panchan Neogi, Atul Chandra Ganguli, Atul Chandra Ghose, Hamendra Kumar Sen, Jitendra Nath Rakshit, Rasik Lal Datta, Nilratan Dhar, Manik Lal Dey, Janendra Chandra Ghosh, Prafulla Chandra Guha and N. Adhikary. Prof. Ray is equally proud of Janendra Nath Mukherjee, Satendra Nath Bose, Pulin Behari Sirkar, Meghnath Saha, Biman Behari Day, Prafulla Chandra Mitra, Priyadarajan Ray, Janendra Nath Ray and Jogendra Chandra Bardhan who studied under him for their undergraduate courses. These scholars have distinguished themselves with their meritorious work, receiving international recognition, and most of them are to-day occupying the professorial chairs in several colleges and Universities in India.

Dr. Ray's activities were not merely confined to the experiments carried out in the chemical laboratory but his knowledge of chemistry led him to establish what is now known as the Bengal Chemical and Pharmaceutical Works Ltd. at Calcutta for the manufacture of drugs and chemicals. It is striking to find that these works which were started in a small house with a meagre capital of Rs. 800/—, are now spread over an area of 60 acres employing 2000 men and their present assets amount to half-a-crore of rupees. In this enterprise Dr. Ray was assisted by his friends, chiefly by Amulya Charan Bose and Satis Chandra Sinha in the early stages of the evolution of the works. To-day the various departments of the works are looked after by expert chemists who are Dr. Ray's students and they, under his able guidance, have succeeded in raising the works to their present status.

But while engaged in the laboratory work Dr. Ray devoted his time equally to studies. Being gifted with the art of writing, he has published several books on scientific subjects both in English and Bengali. His monumental publication is the History of Hindu Chemistry the first volume of which appeared in 1902 and the second one five years later. In these two volumes Dr. Ray has shown that Indian alchemy is of an indigenous origin the ancient Hindus, for example, were acquainted with the processes of sublimation and distillation, could distinguish between mild and caustic alkalis and identify the metals by the colouration of the flame etc. These volumes won for him appreciation both from India and from other parts of the world. The book was reviewed in glowing words by eminent persons in most

of the Journals and papers in India and Europe. Berthelot remarked, 'A new and interesting chapter has been added to the History of Science and human thought.' The University of Durham conferred upon him the honorary degree of D. Sc in 1912 chiefly in appreciation of the History of Hindu Chemistry.

In 1924 Dr Ray with the assistance of Dr. J. N. Mukherji, Dr J. C. Ghosh and Dr S. S. Bhatnagar succeeded in laying the foundation of the Indian Chemical Society of which he is the foundation Fellow and a Patron. The Society elected him as its first president and availed of his vast experience and knowledge in guiding its working in its early life.

On account of his meritorious work and distinguished career Prof. Ray has been honoured from time to time both by the Government and the scientific organisations in India. The University of Calcutta conferred upon him the Honorary degree of Ph D in 1908. The Government of India honoured him with the title of C. I. E. in 1912 and with Knighthood in 1919. The Indian Science Congress elected him as its president in 1920 and various Universities in India invited him to deliver an address at their convocation meetings. H. E. Armstrong has remarked in an article to Nature "Our recognition of Ray's Services, as chemist, as teacher, as historian and as a founder of a great national school of scientific inquiry, is long overdue—it is nothing short of a reproach to our Royal Society that it should hitherto have been so narrow in its outlook as not to include his name in the roll of Fellowship"

Although Prof. Ray's life is full of activities of a scientific character it is noteworthy to find that he gave his fullest share to the activities outside the test-tube. He has been seen working energetically with the rescuers in times of floods and famines. Being a rationalist in his views, he has ever taken a keen interest in reforming the social shortcomings in communal and religious bodies

Prof. Ray is a living embodiment of the maxim 'Plain living and high thinking'. Being a man of ascetic disposition he is ever ready to benevolently help the poor with his purse. His earnings as professor and gains from the Bengal Chemical and Pharmaceutical Works are spent on charities. Mr. Padmuni Mohan Neogy writing about the philanthropy of Prof. Ray in the Indian World says, "... How often have we seen wretched young men, wretched on account of poverty, going up into his laboratory room where they laid bare their heavy bosoms, and he the father of them all, fondling with all the affection as though they were his own...." Like a true Guru, Acharya Ray, as he is usually called, has not only helped his students with money but has spent the best part of his life in training them. He considers these



young workers to be the richest treasure which he could bequeath to the scientific world.

Poor in health—dyspepsia and insomnia being his chronic complaints—Prof. Ray takes every day what he calls constitutional walks and is full of vigour. Besides devoting his time to other activities which are engaging his attention at present, Dr. Ray, now seventy-two years of age, still pursues his scientific researches and one can find a paper by him along with his pupil in the recent issues of the Journal of Indian Chemical Society. Let me end this short account of Dr. Ray's life—an account which is by no means an exhaustive one—with a prayer to the almighty "May he live long to inspire us with his example and precept."

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## AN INDIAN HYGIENE MUSEUM

By

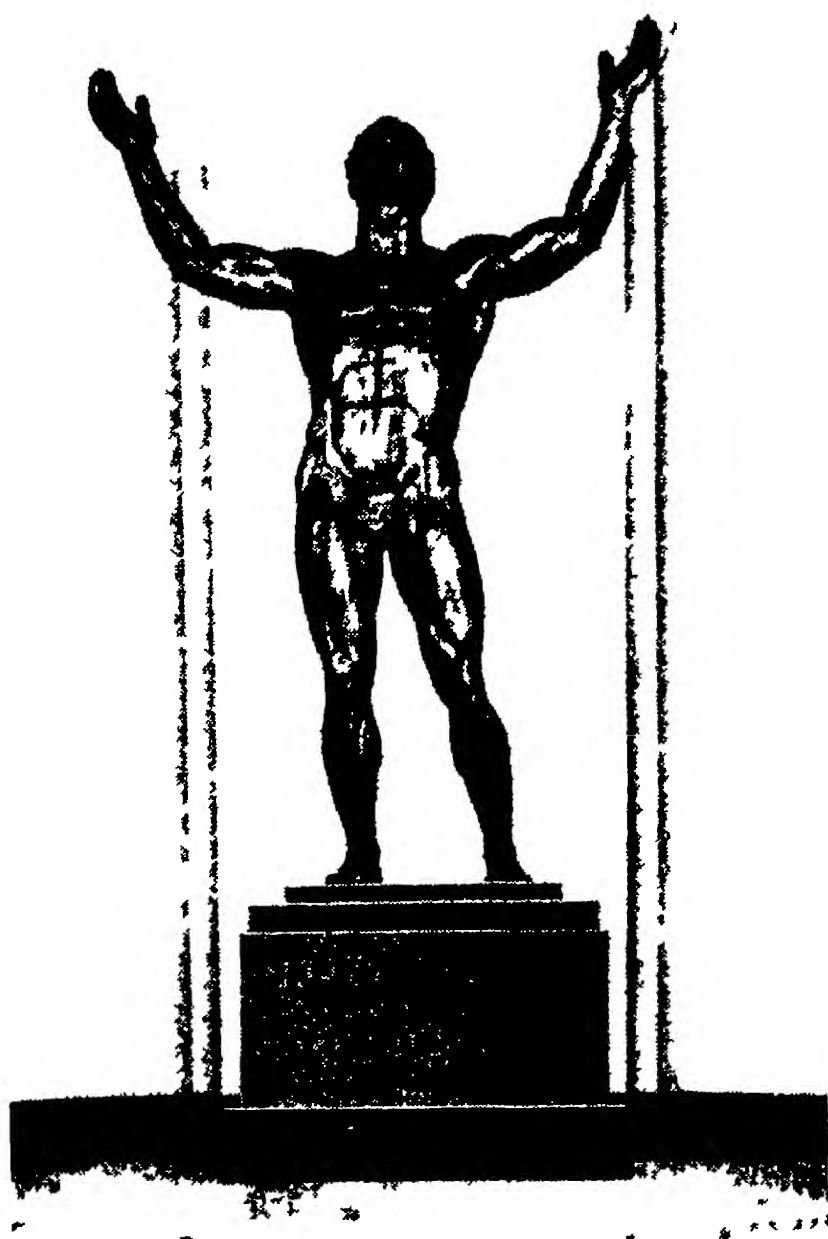
GILBERT J FOWLER, D Sc., F.I.C.

In one of those fateful years when the war clouds were already banking up on the horizon of Europe, the present writer found himself a member of a small executive committee charged with the task of collecting guarantees and donations towards a British pavilion at the great International Exhibition of Hygiene, which was then in course of erection at Dresden

Great difficulties had been encountered in raising money for this British effort, owing in part to the strained political relations which even then existed between the British and German Governments. However, with the assistance of Sir Thomas Barlow, Physician to King Edward the Peacemaker, and his distinguished confrère Sir Lauder Brunton, these difficulties were eventually overcome and a first rate Pavilion was erected in a prominent position in the exhibition grounds. In this building were set out valuable exhibits illustrating the progress of Hygiene and Medicine in Great Britain. Actually a surplus of funds was realised after paying all guarantors, these funds were devoted to the support of institutions concerned with health and physical development.

While the Exhibition was in progress the writer was privileged to visit it as a member of a deputation from the Corporation of Manchester, and to study those exhibits in which he was particularly interested. Among these, memory recalls pictures and models showing the progress of urban sanitation through the centuries, the dreadful filth of medieval towns being compared with the cleanliness and brightness of a modern city.

In the spacious hall entitled "Der Mensch" (Man) dominated by a great statue illustrating the physical ideal of *homo sapiens*, were grouped exhibits showing the perfect conditions to be observed from childhood to age, if this physical perfection was to be attained. In those days vitamins were not so much in the foreground, but food values and calories were amply illustrated. In other halls there were exhibits of a more medical nature and concerned less with health than with disease. The utility of these exhibits may perhaps be questioned, though their object no doubt was to warn by fear, if encouragement by the reward of health should be inadequate.



Der Mensch



## INDIAN HYGIENE MUSEUM

Along these halls passed throughout the day, simple studious people, many of them obviously from the countryside, and all of them absorbing earnestly in conscientious German fashion the education set before them.

With these memories in his mind the author was surprised one day to note in *The Times of India* a paragraph describing a proposal for a Hygiene Museum for Bombay based on the Dresden model. He then learned that the Exhibition of 1911 had become a permanent national Museum and a centre from which help of every kind was willingly given to those who might be engaged in similar activities elsewhere.

It was further learned that the prime mover in the Bombay scheme Mr G M Jadhav was educated at the Manchester Grammar School and afterwards became foreign language master there, where dreams and ideals of service had been born in him altogether a strange coincidence. The original idea based on the Dresden model has been extended to include other subjects of general human interest following the plan of the great Museum at Munich which sets out to illustrate the activities of mankind through the ages.

It is now proposed to have not one but eight Museums as follows —

- Indian Hygiene Museum
- Technology and Engineering Museum
- Museum for Sociology and Economics
- Museum for Agriculture
- Science Museum
- Evolution Museum
- Trade and Commerce Museum
- Geography and History Museum

An excellent site has been earmarked on the new Back Bay Reclamation and it remains for all well wishers of India to support the scheme by their interest, work, and financial generosity.

With his experience of the British Pavilion at Dresden in his mind, the writer cannot doubt that if the will is present, needful finance will be forthcoming.

Surely no object can be more worthy than the creation of a centre of enlightenment and mass education of the simple people of the new India, which, in spite of politicians is rapidly coming into being.

Anyone who has had charge in India of a Museum or even of Laboratories in which interesting and novel experiments are going forward will not need to be convinced of the appeal which teaching by the eye makes to ordinary folk of India. The writer must confess that he was sometimes concerned for the amenities of his bacteriological laboratory when it was invaded by happy families of sightseers,

who regardless of the dust of the highway which they brought with them, came in eager crowds from time to time within the sacred precincts

Official reports from the Calcutta and Madras Museums confirm this eagerness for information on the part of the Indian masses

The writer's recollection of the Ancoats Art Museum planted as it was in the most dingy and depressing quarter of Manchester, encourages him to believe in the even greater usefulness of the proposed Indian centre

Just as the Dresden and Munich Museums send out inspiration and literature to all who desire them so will these Museums in Bombay serve to feed smaller centres and thus spread enlightenment throughout the country

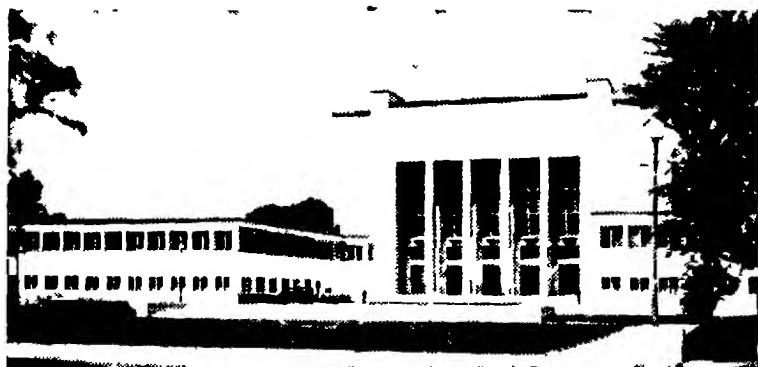
Already more than one energetic Director of Public Health is making use of Models and pictures of all kinds to educate the villagers during Health Weeks and other such public occasions

With the coming of broadcasting these exhibits and the cheap literature which it is also hoped to provide can be explained in simple vernacular language to the rural population

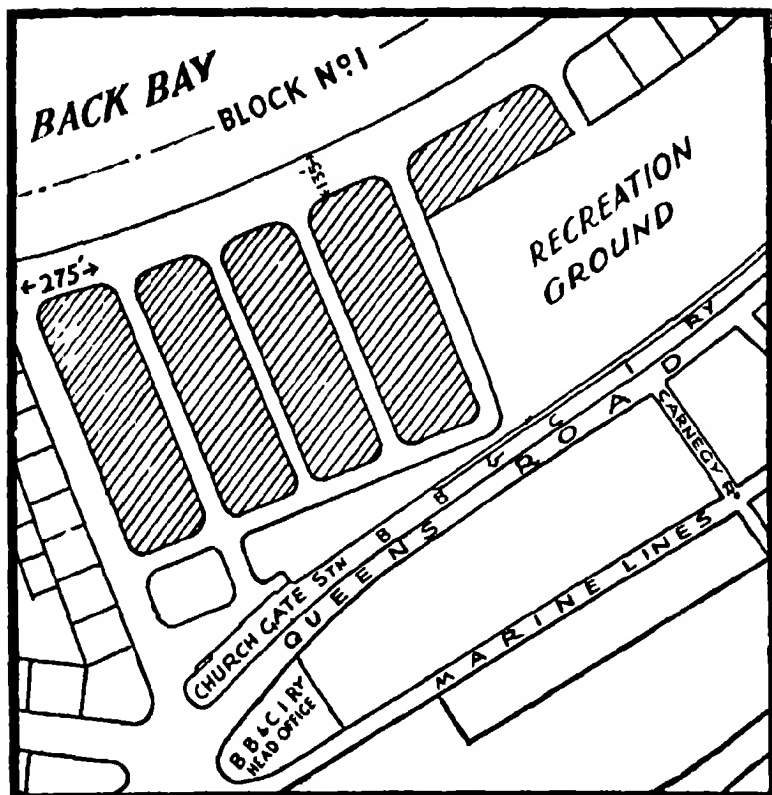
Already through the energy and idealism of the Honorary Secretary of the movement Mr G M Jadhav a beginning has been made with the distribution of such literature

Those interested can obtain pamphlets and other information which they may desire from Mr Jadhav at Parel Bombay

Surely this is an object in which all may unite without distinction of caste creed or race and thus beyond its immediate objective the scheme will play a noble part in spreading the spirit of goodwill which is the greatest need of India and indeed of the whole world to-day



General view of the German Hygiene Museum, Dresden



**The proposed site of the Museum in Bombay.**



## Summaries and Abstracts of M. Sc. Theses for 1932-1933.

1.—*"Some Biochemical Aspects of the Physiology of Sandal"* (*Santalum album* Linn). Being a part of the thesis submitted by MR. Y. V. SREENIVASA RAO, Department of Biochemistry, Indian Institute of Science, Bangalore, for the award of the Degree of Master of Science, University of Bombay.

*Historical and general introduction.*—A historical survey of the growth and spread of sandal in South India is given. The place of sandal in the economy of nature and its economic importance to India are indicated. It represents one of the few parasites which have an economic value.

PART I (A).—*Nature and extent of Parasitism of Sandal as revealed by Inorganic constituents.* The importance of the rôle of mineral nutrients in plant life has been described. The nature and extent of parasitism of sandal from this point of view has been studied.

Control cultures of sandal have established that (1) without a host, sandal continues to have a struggling existence, (2) some host plants are better suited to nourish sandal than others. It has also been found that if sandal is deprived of

its host plants, either by removal or death of the latter, it ceases to put on any visible growth; the leaves turn pale and chlorotic in spite of the rich soil that may be provided. But if a host, more especially of the leguminous type, is reinstalled, the sandal starts growing again, in the course of two to three weeks, the pale yellow leaves turning green and the plant putting on a healthy appearance. Cultural experiments have revealed that sandal is largely dependent upon its host plants for its nitrogen and phosphorus requirements. It has also been found that sandal exhibits a preferential affinity to certain types of host plants, with regard to its haustorial attachments.

PART I (B).—*A Physico-and Biochemical study of the tissue Fluids of Sandal in Relation to the Associated host plant.*—It has been shown how the physico-chemical measurements and chemical composition of the tissue fluids of plants is receiving more and more attention at the present time from physiologists and pathologists.

Physical-chemical measurements of the tissue fluids of the leaves, stems and roots of sandal in association with its hosts, have



revealed that the osmotic pressure of the sandal is always greater than that of its host. This is in conformity with the results of Arthur Harris and J V Lawrence who have shown, in their work on the "Osmotic concentration of the tissue fluids of Jamaican Lorantheae parasitic on various hosts," that the parasite has always a higher osmotic concentration than its host.

Analyses of pot cultured sandal plants nourished by known hosts have shown that the host has a considerable influence on the composition of the sandal sap, thereby rendering the plant more or less open to insect attack. The practical value of this interesting fact is realised if attention is called to the officially accepted theory that insects are the natural vectors of "Spike". By a judicious choice of host plants it should be possible to control the composition of the sap in such a way as to render it distasteful or repulsive to those classes of insects reputed to be vectors of disease.

PART I (C) — *Nitrogen Metabolism of sandal with and without host plant*. Distribution of the nitrogen (in the water soluble portion) in the leaves of sandal with and without host plant has been studied. It is seen that, with the removal of the host plant, the green leaves turn yellow and the tree will have a struggling existence, and this indicates that nitrogen constitutes the limiting factor without which the parasite does not flourish. The total and

the protein nitrogen decrease on removal of host plant due to the poor absorption of nitrogen directly from the soil.

The water soluble nitrogen increases due to proteoclastic degradation of the native proteins and the ammonia nitrogen is also higher due probably to deamination in the case of the sandal without host. A study of the distribution of the hexone bases, has shown that Arginine nitrogen is slightly but distinctly greater in sandal without host. The cystine content on sandal without host is very low. This is very significant in view of the fact that cystine is known to favour the formation and functioning of root hairs.

*Distribution of the Hexone Bases in Healthy and Diseased Leaves of Sandal.* An historical introduction of the spike-disease of sandal has been given from the time when it was first discovered by McCarthy in the year 1899 with a summary of the results so far obtained.

The distribution of the hexone bases in the healthy and spiked sandal leaves has been worked out by two entirely independent methods with a view to determine the nature of the metabolic disturbances which manifest themselves with the onset of the disease.

(i) Van Slyke method as modified by Plummer and Rosedale (1925)

(ii) Kossel's silver-baryta method

The fact that the histidine

fraction occurs in a high proportion is significant in view of its close structural relationship with the physiologically active histamine, which has been found to inhibit the growth and functioning of roots.

**Carbon-Nitrogen Ratios in Healthy and Diseased Tissues of Sandal.** A modified apparatus for the determination of total carbon in plant material by the wet combustion method has been described.

Carbon Nitrogen ratios in healthy and spiked sandal have been estimated with a view to ascertain whether there would be any disturbance in this (C/N) ratio with the onset of the disease when the reproductive activity of sandal is arrested. The results are somewhat erratic and no definite conclusions could be drawn. While in the case of partially spiked plant, the C/N ratio in the beginning is not altered very much.

II.—“*Proteins of Fenugreek*” (*Trigonella Foenum Graecum*) being a part of the thesis submitted by Mr Y. V. SREENIVASA RAO, Department of Biochemistry, Indian Institute of Science, Bangalore, for the award of the degree of Master of Science, University of Bombay.

The globulin and albumin in fenugreek have been isolated and analysed. The globulin (fraction A) is characterised by a surprisingly high content of histidine which is about four and a half times the average amount contained in other

related globulins obtained from leguminous seeds. In this respect the protein has a close relationship with the protamines and histamines which are characterised by a high content of the hexone bases. The albumin (fraction B.) appears to contain phosphorus and sulphur in the molecule. In this respect the composition of this fraction approaches the casein of milk.

III.—*Dilatometric Studies in Enzyme Action* Being a summary of a part of the thesis submitted by Mr. H B SREERANGACHAR, Department of Biochemistry, Indian Institute of Science, Bangalore, for the award of the Degree of Master of Science, University of Bombay.

The kinetics of two closely allied enzyme-substrate systems have been studied in the dilatometer. The course of reaction has also been followed by an entirely chemical method. The possibility of employing this elegant method for a time course study of these two enzyme-substrate reactions has been established.

A new type of dilatometer has been described where the enzyme and the substrate could be mixed in the dilatometer itself, thereby facilitating an investigation of the changes from the beginning of the reaction. The kinetics of the reaction could simultaneously be followed. At lower concentrations of substrate the total contraction

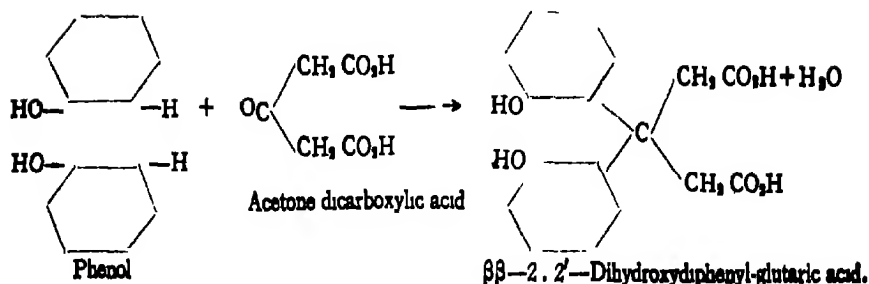
VI.—*Condensation of Phenols and Phenolic Ethers with Acetone Dicarboxylic acid. Synthesis of  $\beta\beta$  substituted glutaric acids.* BY V M DIXIT and G. N. GOKHALE. Being a summary of Part I of the thesis submitted by Mr Gokhale in October, 1932, for the M. Sc degree of the University of Bombay.

Acetone dicarboxylic acid has been condensed with phenols in the presence of various catalysers, the commonest amongst which is conc. sulphuric acid. [See — *Coumarin-4-acetic acids* by Fries and Volk (Annalen, 1911, 379, 90), Dey (Trans. Chem. Soc. 1915, 107, 1606) Dey and Row (J. Ind. Chem. Soc. 1924, I, 110) and Limaye (J. Ind. Chem. Soc. 1927, IV, 159)].  $\beta$ -Substituted glutaric acids by Limaye and Dixit (vide Proc. Ind. Sc. Congress 1930, 167), Limaye and Bhavs (J. Ind. Chem. Soc. 1931,

VIII, 137) and Dixit (J. Ind. Chem. Soc. 1931, VIII, 787). The acetone dicarboxylic acid acts in the enolic form in these reactions.

A new compound was prepared by condensing phenols (2 mols) with acetone dicarboxylic acid (1 mol) in the presence of dilute sulphuric acid (75 p. c.). It was a crystalline dibasic acid (Formula  $\text{—C}_{17}\text{H}_{18}\text{O}_6$ , Eq. Wt. 158 and M P  $234^\circ$ ) (with decomp) which formed insoluble copper and lead salts. Aqueous solution of the acid gave a bluish green coloration with ferric chloride. Similar new acids were obtained from o-cresol, quinol and p-cresylmethyl ether. Phenol gave the greatest yield.

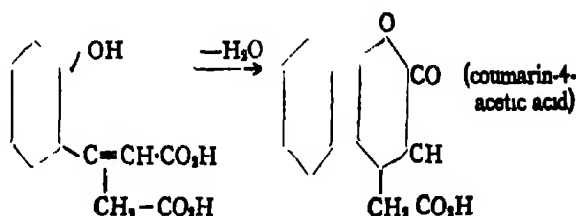
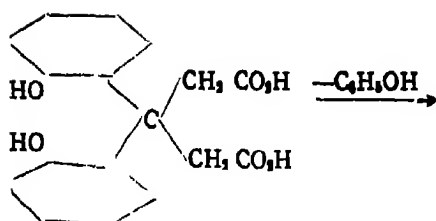
The constitution of  $\beta\beta$ -2,2'-dihydroxydiphenyl glutaric acid is proposed for the new acid from phenol. The condensation is assumed to take place as follows:—



The acetone dicarboxylic acid acts in the ketonic form. The results of the following reactions bear out the given constitution —

(1) Action of conc. sulphuric acid at  $50^{\circ}$ - $60^{\circ}$  :—The compound

breaks up almost quantitatively into coumarin-4-acetic acid, identical with that prepared by Lumaye (*loc. cit.*) and phenol. The reaction is explained as :—



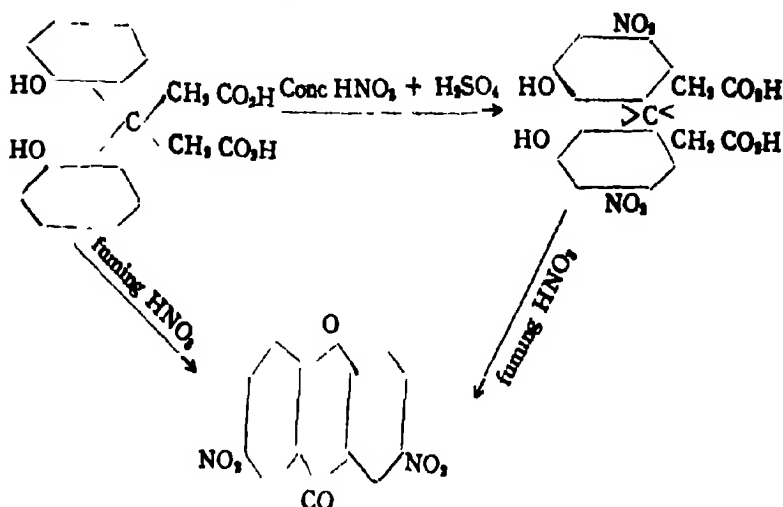
The intermediate glutaconic acid cannot be isolated [Dey, (*loc. cit.*)] except in the decomposition of the corresponding glutaric acid obtained from p. cresyl-methyl-ether.

(2) Action of nitric acid.—On

heating the new substance with conc. nitric acid in the presence of a small quantity of sulphuric acid in cold, a dinitro derivative was obtained.

Heating this dinitro derivative

or the original glutaric acid with a small quantity of picric acid. The reaction can be represented as,—



(3) Action of KOH.—Fusion of the glutaric acid with moist caustic potash at 180° gave 2, 2' dihydroxybenzophenone, identical with that obtained by Richter [J. Pr. Chem. 1883, (2) 28, 285].

(4) Knoevenagel condensation.—Unlike the esters of coumarin-4-acetic acids, the ester of the new acid or the acid itself did not yield any condensation product with salicylic aldehyde in spite of several attempts with usual precautions.

(5) Synthetical reactions.—The dimethyl ester of the new glutaric acid formed the corresponding apocamphoric ester by condensing with dimethyl oxalate according to the method of Kompapa (Trans. Chem. Soc. 1911, 99, 2020) and it also condensed with dimethyl phthalate according to the method of Dieckmann (Ber.

1899, 32, 2227).

Besides these, the new glutaric acid formed a number of characteristic derivatives. The corresponding glutaric acids obtained by condensing acetone dicarboxylic acid with o-cresol, quinol and p-cresylmethyl ether respectively showed analogous equivalent wts., analytical data, salts and behaviour with conc. sulphuric acid.

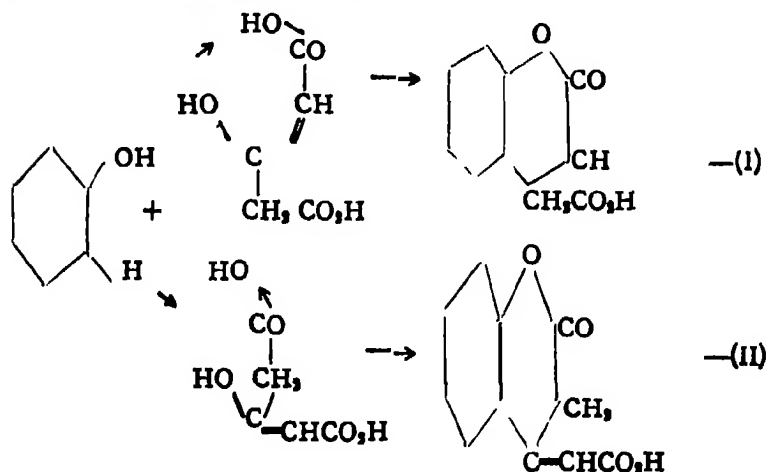
In converting the ββ-2: 2'-dimethoxy-4 4'-methyl-phenyl glutaric acid, which is obtained from p-cresyl-methyl ether, into the corresponding 6-methylcoumarin-4-acetic acid by sulphuric acid, the intermediate β-2-methoxy-5-methylphenyl glutaconic acid was isolated. This on keeping in conc. sulphuric acid changed to the 6-methyl-coumarin-4-acetic acid.

The work is being continued.

VII.—*Condensation of phenols, with acetone dicarboxylic acid, Anhydrides of  $\beta$ -2-hydroxy-phenylglutaconic acids.* By V. M. DIXIT and G. N. GOKHALE.

Coumarin-4-acetic acids have been prepared by condensing phenols with acetone dicarboxylic acid, in the presence of conc. sulphuric acid. [See:—Dey (Trans. Chem. Soc. 1915, 107, 1606). Dey and Row (J. Ind. Chem. Soc. 1924,

I, 110), Limaye (J. Ind. Chem. Soc. 1927, IV, 159) and Dixit (J. Ind. Chem. Soc. 1931, VIII, 787)]. In some of his reactions, Dey has obtained tautomers (I and II) of the same coumarin 4-acetic acid supposed to be formed at the same time due to the two different ways in which the acetone dicarboxylic acid may act. The reaction is represented as follows.—



Transformation of (II) to (I) was supposed to take place in the process of crystallisation which invariably caused a considerable change in the melting points. The two forms had the same equivalent weight and analytical data and both produced the corresponding 4-methylcoumarin when heated at their m. pts. Other experimental evidence to show the existence of (II) has not been recorded and the conversion of (I) to (II) has not been carried out.

With the object of studying the reaction in details, phenol and the

three cresols were condensed with acetone dicarboxylic acid on the lines described by Dey and Row (loc. cit.) as the results from this method and that of Dey (loc. cit.) were identical. The crude product of each of these reactions, when fractionally crystallised yielded two different compounds (A) and (B) which were partly transformed into one another on long exposure to air.

The substance (A) of lower m.pt. :—

(1) Crystallises in long needles soluble in hot water, dilute alcohol,

ether and in sodium bicarbonate solution with effervescence. The original compound is recovered on acidifying this solution.

(2) Does not give any coloration with ferric chloride and does not form any definite compound with (i) acetyl chloride or acetic anhydride, (ii) benzoyl chloride, and (iii) oxidation by chromic acid in cold.

(3) Yields almost theoretical quantity of 4-methyl-coumarin when heated at its melting point.

(4) Forms the solid ethyl ester which in turn condenses with salicylic aldehyde in the presence of piperidine to produce the corresponding dicoumaryl (see Dey and Row). In short the substance (A) agrees well with the corresponding coumarin-4-acetic acid, found in literature.

The substance (B) of higher melting point :—

(1) Crystallises in broad pris-

matic needles, insoluble in water and dilute alcohol, soluble in alcohol, acetone and chloroform. Insoluble in sodium bicarbonate unless being in contact with it for a long time.

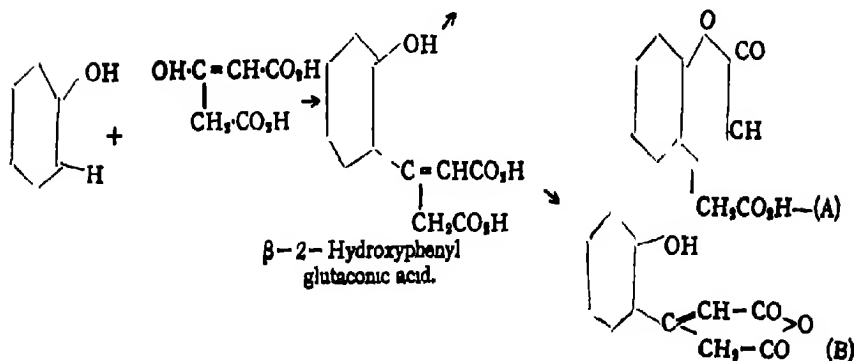
(2) Gives, in alcoholic solution, reddish coloration with ferric chloride.

(3) Can be titrated in alcoholic solution with alkali and has the same equivalent weight and analytical data as those of substance (B).

(4) Does not form an ester and does not condense with salicylic aldehyde under dry conditions.

The compound (A) can be converted into (B) by keeping it in contact with conc. sulphuric acid. The reverse change proceeds on hydrolysis of (B) by alkali.

The compound (B) is supposed to be the anhydride of the corresponding ortho substituted glutamic acid, formed as follows :—



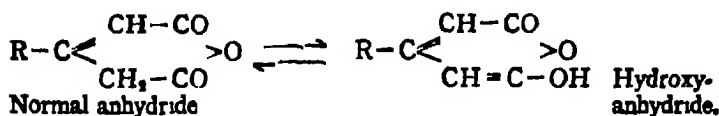
The intermediate glutamic acid is known to be incapable of free existence.

The following evidence is found in literature to justify this course

of the condensation:— (1)  $\beta$ -substituted glutamic acids have been prepared by condensing phenols and phenolic ethers with acetone dicarboxylic acid (See

Limaye and Bhawe, J. Ind. Chem. Soc. 1931, VIII, 137. Dixit, J. Ind. Chem. Soc. 1931, VIII, 787 and Limaye and Gogate Proc. Ind. Sc. Congress 1932, 233). The corresponding coumarin-4-acetic acids were also found as by-products in these reactions.

(2) The substance (B) acts as a



The following experiments were further carried out with the substance (B), and their results agree with the constitution assumed for it.

(1) Benzoylation - Action of benzoyl chloride on the compound in solution with pyridine produces a neutral dibenzoyl derivative which is hydrolysed by alkali to the corresponding coumarin-4-acetic acid.

(2) Elimination of  $\text{CO}_2$  :— By decomposing the dry compound under specially dry conditions, and reduced pressure, a phenolic substance results which sublimes and lowers the m. p. of the corresponding 4-methylcoumarin when mixed with it.

(3) Oxidation :—Oxidation of the substance in solution with acetic acid by chromic acid yields the corresponding ortho-hydroxy benzoic acid.

(4) Action of acetic anhydride in the presence of sodium acetate on the substance gives a crystalline acidic compound which is supposed to be formed according to the

monobasic acid on account of its transformation into the "Hydroxy anhydride" due to the mobility of a hydrogen atom as explained by Thorpe [See Thorpe and Thole (Trans. Chem. Soc. 1911, 99, 2187) and Thorpe and Bland (Trans. Chem. Soc. 1912, 101 867)].

reaction described by Gabriel and Neumann (Ber. 1893, 26, 951). The nature of this reaction is still under investigation.

The results obtained so far seem to indicate that the crystallisation of the crude product of higher m. p. into coumarin-4-acetic acid of lower m. p. as reported by Dey in some cases, may be due to the partial conversion of the substance of (B) type into that of (A) under those conditions.

Further work is in progress.

IX.—*Latent Instability in the Atmosphere revealed by some Indian Tephigrams.* By Miss M. M. PARANJPE, B. Sc.

By the application of the curve of saturation temperatures termed estegram (S. T. gram) suggested by Dr. C. W. B. Normand, for indicating humidity from the thermodynamic point of view, about 250 sounding balloon records over Agra, Poona and Hyderabad during 1929 to 1931 were examined from the point of view of latent instabi-



lity. Typical cases are described and limitation of the records on account of hair hygrometry considered. The conservative property of equivalent potential temperature is examined and in this connection a review is made of the various types of adiabatic diagrams and their bearing on equivalent potential temperature.

Sources of air samples relating to each individual record either exhibiting marked latent instability or no latent instability were investigated by tracing trajectories of upper air movement from the results of pilot balloon flights of the Indian net work of stations at various levels. Weather notes for all days of soundings bear out what would be expected namely that absence of latent instability is associated with dry, fine weather with occasional high clouds of non-convective type and latent instability with convective types of clouds like cumulus and cumulo-nimbus or rain or thunder or thunderstorms.

In general, marked latent instability is associated with incursions of oceanic air of tropical or equatorial origin having high equivalent potential temperature of the order of  $340^{\circ}$  to  $350^{\circ}\text{A}$  or more and decreasing with height, and that absence of latent instability is associated with continental air having relatively low E. P. T. of the order of  $320$ – $330^{\circ}\text{A}$  increasing or remaining approximately constant with height. From the general circulation of upper air currents over India, this explains

the comparative scarcity of latent instability in the winter both at Agra and Poona and Hyderabad as contrasted with the remaining part of the year.

#### X.—*Studies in Ferric Hydroxide Sol* By S. K. BORKAR and B. N. DESAI.

Measurement of charge on ferric hydroxide sol has been carried out under various conditions *e.g.*, with progress of dialysis, in presence of electrolytes, from the point of view of critical potential, with progress of dialysis and with different dilutions. Simultaneous measurements of charge and viscosity with progress of dialysis have also been made.

It is found that with progress of dialysis the charge first increases, reaches a maximum, and then decreases. The stability is found to decrease continuously. There is an initial increase in charge on the addition of small quantities of electrolytes such as  $\text{HCl}$ ,  $\text{KCl}$  and  $\text{FeCl}_3$ . It is also found that various samples of the sol coagulate at the same value of the charge—the critical charge—except in the case of  $\text{HCl}$  where the value is slightly higher.

On dilution it is found that sols dialysed for a period shorter than what corresponds to the maximum in the cataphoretic speed-dialysis curve, behave in one fashion; while those that are dialysed for a longer period behave differently.

Measurements on viscosity and charge show that neither the view

of Dhar (smaller viscosity, smaller hydration and greater charge; and greater viscosity, greater hydration and smaller charge) nor of Smoluchowski (greater charge, greater viscosity, and smaller charge, smaller viscosity) can individually explain the results.

**XI.—Action of Nitric Acid on Tin.** By G. S. KASBEKAR and A. R. NORMAND.

The reaction between tin and nitric acid under varying conditions has been studied by estimating all the products formed during the reaction, whether in the dissolved or in the gaseous state. It has been shown that during the above reaction in addition to the formation of stannous and stannic salts, hydroxylamine, ammonia, nitric oxide, nitrous oxide and nitrogen are formed. Neither nitrous acid nor hydrazine were formed under the conditions studied. The effect of various catalysts on the reaction was also studied.

It has been pointed out that the variations in the stannic tin and the gaseous reduction products of excess nitric acid go hand in hand, whereas the variations of stannous tin in solution are similar to the variation of the reduction products in solution, namely hydroxylamine etc.

In an attempt to explain the reduction of excess nitric acid not only has it been shown that nascent hydrogen could be the probable reducing agent, but it has

further been suggested that the nascent hydrogen produced by the dissolution of tin in nitric acid may be of two different activities, the dissolution of tin to the stannous condition producing hydrogen of one activity while the dissolution of tin to the stannic condition producing hydrogen of a different activity.

**XII—Studies in Solubility.** By P. G. DESAI and A. M. PATEL.

Part. I. Effect of polar and non-polar solvents on the solubilities of some organic acids.

The solubilities of benzoic, cinnamic, salicylic, phthalic and succinic acids have been determined in polar and non polar solvents. In the case of non-polar solvents, the solvent action decreases with the increase in the polarity of the solute, the solubilities of phthalic and succinic acids being negligible in these solvents. The order of solubility is in accordance with the polarity of the solvents in case of slightly polar solvents, while in case of more polar solvents, the order is not well defined. Ideal solubilities of benzoic, cinnamic and salicylic acids are approached in ethyl alcohol, while those of the more polar phthalic and succinic acids are approached in methyl alcohol. Chloroform and acetone behave abnormally. It has been inferred from the solubilities of acids in water, nitrobenzene and alcohols that, benzoic cinnamic and salicylic acids form loose alcoholates with the solvents,

while succinic and phthalic acids form hydrates with water.

Part II The solubilities of benzoic and salicylic acids in mixtures of solvents.

The solubilities of the two acids were determined in a number of binary mixtures. It is found that when both the components of the mixtures are non-polar, the solubility composition curves are almost straight lines, whereas in case of mixtures of chloroform with aromatic hydrocarbons, the curves are convex towards the composition axis. In case of mixtures of acetone with non-polar liquids, the curves are concave towards the composition axis. In case of mixture of alcohols with non polar liquids and with nitrobenzene, the solubility increases, reaches the maximum and then decreases. The same is the case with mixture of nitrobenzene with the non-polar solvents. The results have been explained on the basis of association and de association of molecules of the solvents when in presence of one another.

Part III. Relation between adsorption and solubility.

The adsorption of benzoic acid by animal charcoal, from mixture of (i) two non-polar, (ii) polar and non-polar and (iii) two polar solvents was determined. Adsorptions from non-polar liquids is greater than that from polar liquids. It is found that an inverse relation exists between solubility and adsorption. In case (i), the adsorption-composition curves are almost straight lines; while in the two

remaining cases, minima are generally obtained on the adsorption-composition curves. It has been shown that in most cases where maxima are obtained on the solubility-composition curves, minima are obtained on the adsorption-composition curves.

Part IV Viscosities of binary mixtures.

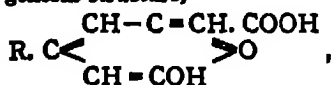
The viscosities of the mixtures of (i) two non-polar, (ii) two polar (iii) polar and non-polar liquids have been determined. It has been shown that in case of first type, almost straight lines with slight sagging are obtained. In mixtures of second type, viscosity-composition curves are convex to the composition axis with a minimum point in the case of n-propyl alcohol-nitrobenzene system. In case of the third type, the curves are convex to the composition axis, with a minimum in the case of benzene n-propyl alcohol system. An attempt has been made to relate viscosity-composition curves to the solubility-composition curves.

XIII.—*The Action of Acetic Anhydride and Sodium Acetate on the Anhydrides of  $\beta$ -Glutaconic Acids The formation of  $\beta$ -Aryl-Acetic Acids with an Addendum.* By VISHNU MAHADEO BHAVE, M. Sc.

Being the summary of a thesis submitted in June 1932 from the Ranade Industrial and Economic Institute, Poona (4).

(1) By the action of acetic anhydride and sodium acetate on

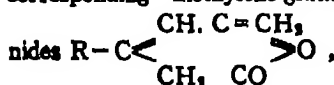
the anhydrides of  $\beta$ -aryl-glutaconic acids, enolic forms of the  $\beta$ -aryl-glutaconyl-acetic acids of the general structure,



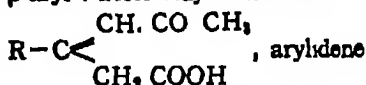
have been prepared for the first time,

[R = (a) anisyl, (b) phenyl, (c) 'methoxy orthocresyl, (d) methoxy para-cresyl, (e) methoxy meta-cresyl, and (f) ortho-methoxy-phenyl].

(2) Their constitution has been determined by the isolation of the corresponding methylene-glutaconides

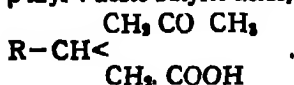


$\beta$ -aryl- $\gamma$ -aceto-vinylacetic acids



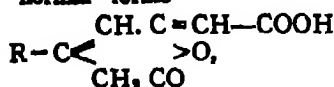
ketones  $\text{R} \cdot \text{C} \begin{array}{c} \text{CH} \cdot \text{CO} \cdot \text{CH}_3 \\ \text{CH}_3 \end{array}$  and

$\beta$ -aryl- $\gamma$ -aceto-butyric acids,



(3) A parallelism between this reaction and the Gabriel's extension of Perkin's reaction to Phthalic anhydride has been established.

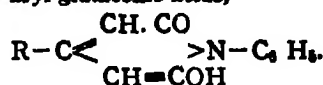
(4) The 'enolic' or 'hydroxy' glutaconyl-acetic acids have been converted into their 'keto' or 'normal' forms



thus incidentally confirming Thorpe's view that glutaconic anhydrides exist in the 'enol' i.e., the

hydroxy pyrone form.

(5) The reaction has been tried, on the hydroxy anils of aryl-glutaconic acids,



(6) It has been suggested that the possibility of the condensation of acetic acid with  $\beta$ -aryl-glutaconic anhydrides may be due to conjugation.

(7) The *addendum* consists of a continuation of the work published in the Journal of The Indian Chemical Society, 1931, 8 137, by Limaye and Bhawe, and the  $\beta$ -(4-methoxy-phenyl)-and  $\beta$ -(4-methoxy-3-methyl-phenyl)-glutaconic acids have been studied in more detail.

(8) Many functional derivatives like esters, semicarbazones, oximes, anilides, benzoyl-derivatives etc, of the main products have been prepared (in all some 90 new substances).

D. B. L.

XIV — *Study of the pectic changes in the potato tubers at different stages of growth and in storage.* By S. D. AGNIHOTRI. (Dept. of Botany, Royal Institute of Science, Bombay.)

The study of the pectic changes in potatoes at different stages of growth, maturity and of senescence during storage is undertaken as it appeared from the survey of the literature on the pectic constituents of fruits and other plant-

organs that the softening of the tissue and its ultimate decay was due to the pectic changes occurring in them. The problem of potato storage is of economic importance in Western India and in spite of the efforts of the various workers there is no unanimity of opinion about the causes of decay of potatoes when stored during the summer months.

The method of Caree and Nanji modified slightly for the needs of this investigation for extracting and estimating different pectic constituents are employed. The free soluble pectin, protopectin, middle lamella pectin, and total pectic materials are determined and expressed as calcium pectate number for the tubers at different stages of growth and at short intervals after storage till the tubers are completely rotted.

The free soluble pectin, protopectin, middle lamella pectin and total pectins begin to rise as growth proceeds and the increases become smaller at maturity.

The free soluble pectin increases and the other three pectic constituents decrease as the age advances, and as the rotting sets in.

The downgrade changes begin to occur in storage conditions and they are responsible for the softening of the tissue which is caused by the separation of the cells due to loss of insoluble proto-pectin, and middle lamella pectin from the cell walls. The bacteria and other organisms get a footing as it were when the tissues soften

and hasten the rotting of the tubers.

The study of the effect of temperature on the pectic changes in mature tubers shows that the downgrade changes are much accelerated as compared to the similar changes in tubers stored at room temperatures.

All tubers pass through the same sequence of pectic changes and during the hot weather they are, like all chemical reactions, accelerated.

The practical side of the potato storage is discussed in view of the results obtained and the lines on which further investigation should be undertaken are indicated.

XV.—*The Kinetics of Heterogeneous Organic Reactions: A study of the Benzoin Reaction.*

BY D. R. NADKARNI, B. SC.,  
Royal Institute of Science,  
Bombay

It is not clear from the literature whether potassium cyanide and benzaldehyde in the absence of any other substances can yield benzoin. It has now been shown that pure benzaldehyde and pure potassium cyanide can yield benzoin but the reaction is readily inhibited by substances such as quinal and alkali halides, which are also negative catalysts in the oxidation of benzaldehyde. The conflicting results in the literature have thus been traced to their source, as the alkali halides are likely impurities in potassium cyanide. The kinetics of this reaction have been

studied at 100°C and at room temperature, and may be represented by the following equation :

Rate of formation of benzoin =  $K_1 [C_6H_5CHO]^2 [benzoin] + K_2 [KCN] [C_6H_5CHO]^2$ . It is suggested that two reactions take place :

(a) A homogeneous reaction between a trace of potassium cyanide dissolved in benzaldehyde. This reaction is autocatalytic and is not affected by inhibitors in the same manner as the heterogeneous reaction.

(b) A heterogeneous reaction between solid cyanide and benzaldehyde, the cyano-ion on the surface of the crystalline cyanide being effective in bringing about the reaction. This reaction is inhibited by the negative catalysts which are adsorbed on the surface of the solid cyanide.

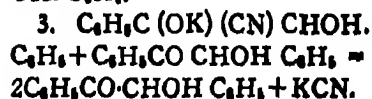
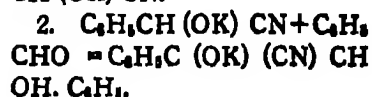
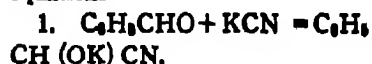
The kinetics of the reaction in presence of water have also been investigated. The rate of the homogeneous reaction is unaffected but the reaction with solid cyanide is replaced by reaction with cyanolons. This heterogeneous reaction between the dissolved cyanide and benzaldehyde is more rapid than that with anhydrous cyanide.

As the quantity of water is increased the dissolved cyanide is extracted from benzaldehyde and the homogeneous reaction ceases.

Inhibitors act in presence of water but their effect is greatly reduced. In fact water is decidedly a catalyst for the reaction probably because it induces the formation of a cyano-ion,

Current theories of the benzoin reaction which have assumed that the presence of water is essential for it to proceed are discussed in the light of the above results. It is pointed out that under anhydrous conditions the potassium cyanohydrin compound itself reacts whereas in presence of water the cyano-ion brings about the reaction.

The necessity for the presence of benzoin before the homogeneous reaction can proceed may be explained by the following series of equations :



S. M. and D. N.

#### XVI.—*Cellulose from rice straw.*

By B. B. SARDESHPANDE.

This work was undertaken to work out proper data pertaining to the yields of cellulose from Bombay rice straw under various conditions of alkali concentration, temperature and time of digestion and to find out whether it is possible to prepare paper and allied products from the cellulose obtained from Bombay rice straw.

The investigation has shown that Bombay rice straw contains 48 to 55% total celluloses. Out of these 34 to 37% is alpha cellulose and the rest beta and gamma celluloses. In actual mill practice,

therefore, the yield of cellulose from Bombay rice straw should be about 36 to 37%. To produce good quality of cellulose the straw should be digested in 3% alkali solution at  $140^{\circ}\text{C}$  for  $1\frac{1}{2}$  hours. Total alkali required for complete digestion of the straw is 10.5%. Total amount of bleaching powder required for the bleaching of the cellulose is 4.5% calculated as  $\text{CaOCl}_2$ . The fibres of rice straw resemble those of esparto in many respects. As the fibres of rice straw are shorter in length they have to be mixed with a small percentage of cellulose with longer fibres for ordinary paper manufacture. Samples of paper have been prepared from the cellulose obtained during the investigation and these have been favourably reported upon by paper makers

M. S. P.

#### XVII.—*Starch and oil from Jowar.* By K. P. SHAH.

This work was undertaken to find out a suitable process for the extraction of starch from Jowar and to study the properties of the starch and the nature of the by-products.

The investigation has shown that sulphurous acid process is a most suitable one for producing starch from Jowar. The yield of the starch by this process is 52% of the total weight of Jowar taken. It was found difficult to separate the germs completely from the grain by floatation. It is therefore necessary to work out some other

process for the separation of the germs. The gelatinisation temperature of jowar starch has been found to be  $67^{\circ}\text{C}$ . Jowar starch granules are polygonal in shape and larger in size than those of the maize and rice starch. The starch gives a good paste without any grit and acted as a good binding material for the size. The starch gets desized very easily. The viscosity measurements showed that jowar starch resembled wheat starch in its paste forming qualities. The waste bran obtained after separation of starch from jowar contains about 11% protein matter. The oil obtained from the germs of the jowar grain is a semidrying oil resembling maize oil in its properties. It had the following analytical characteristics — Colour, Golden yellow, Solidifying point  $8^{\circ}$  to  $9^{\circ}\text{C}$ , Specific gravity 0.910 at  $28^{\circ}\text{C}$ , Refractive Index 1.467 at  $28^{\circ}\text{C}$ , Sap. value 173.2; Iodine value 126.8; Unsaponifiable matter 7.9%, Iodine value of the mixed fatty acids 130, Neutralisation value of the mixed fatty acids 166.5, Sap. of the mixed fatty acids 186.1.

M. S. P.

#### XVIII.—*Hydrogenation of Common Indian oils.* By B. S. KANVINDE for the M. Sc. degree of the University of Bombay.

This work was undertaken to work out a suitable data for the manufacture of tallow substitute from vegetable oils by studying the

hydrogenation of Indian oils treated alone or in mixture in various proportions.

Ground oil, linseed oil, castor oil coconut oil and cotton seed oil were hydrogenated under various conditions of catalytic concentration using both supported and unsupported catalyst. From the results obtained it has been found that a mixture of groundnut oil (pea-nut oil) coconut oil and castor oil in a definite proportion will give on hydrogenation a product which has almost the same physical and chemical characteristics as the animal tallow. The investigation has further shown that the temperature of reduction has considerable influence on the activity of the supported catalyst. The melting point of groundnut oil at any particular degree of hydrogenation is the same irrespective of the nature and concentration of the catalyst used during the hydrogenation. Mixture of oils consisting of glycerides having similar constitution have in general a mean course of behaviour during hydrogenation in relation to individual oils.

M. S. P.

**XIX.—The Photo-reduction of Ferric Chloride in Alcoholic Solutions:** By P. S. LIMAYE B. Sc., The Royal Institute of Science.

The photo-reduction of ferric chloride in alcoholic solutions has been studied in sunlight and in

artificial light. It has been found that in both the cases the reduction takes place in two stages: the order of the reduction in the first stage in the two cases is zero molecular. But in the second stage it is unimolecular in the sunlight and zero molecular in the artificial light. The extinction coefficient measurements of the solutions exposed to artificial light also show a sudden decrease in value after sometime. The change in the stage of the reduction from the first to the second in the above case is not due to the formation of colloidal ferric hydroxide as it has been found to retard the reduction in both the stages. The conductivity of solutions of ferric chloride exposed to sunlight also indicates that a change in the mode of reduction takes place sometimes after the exposure. The results are explained on the assumption that molecular species containing ferric ions are formed and they bring about the change in the mode of the reaction.

The quantum efficiency for solutions of concentrations between 0.1 M and 0.2 M lies between 1 and 3 at 30° for radiations lying in the visible region and it increases with (i) temperature, (ii) concentration of the solution and (iii) frequency of the incident light.

S. M.

**XX.—Studies in Titanium Dioxide Sol.** By Miss OLIVE JOSEPH B. Sc., The Royal Institute of Science.



The coagulation of the titanium dioxide sol by sodium and magnesium chlorides has been followed by the thermopile method during the progress of the dialysis of the sol. The coagulation velocity curves are 'S' shaped for sols dialysed up to ten days; sols dialysed for longer time do not show the autocatalytic nature of the coagulation process. Smoluchowski's equation applies to the coagulation of the titanium dioxide sol for only a limited range of the concentration of the coagulator.

The changes in the viscosity of the sol, dialysed and diluted to different extent, are measured with the progress of time when the sol is coagulated by mono, di and tri-valent electrolytes and mixtures of these electrolytes with non-electrolytes (methyl, ethyl and n-propyl alcohols). In each case the viscosity increases to a maximum value and then begins to decrease. With electrolytes alone the time-viscosity curves are straight rising ones but in the presence of alcohols which exert peptising influence, these curves are 'S' shaped.

S. M.

**XXI.—Studies in Ceric Hydroxide Sol.** By M. V. NABAR, B.Sc., Royal Institute of Science.

The coagulation of the ceric hydroxide sol, dialysed and diluted to different extent, has been studied when the sol is coagulated by sodium and magnesium chlorides and by a mixture of sodium chlo-

ride with alcohols (methyl, propyl and amyl) and solutions of sugars (cane sugar and glucose). The coagulation velocity curves are 'S' shaped for impure and the concentrated sols and steep for those diluted and dialysed for a long time. Smoluchowski's equation applies to the coagulation of the ceric hydroxide sol up to a limited range of the concentration of the coagulator. The alcohols sensitise and the sugars protect the coagulation of the sol by electrolytes: these actions increase as the sol gets purer. The sensitising action of alcohols increases as



Cane sugar and glucose act as protecting agents and the protective action of cane sugar is greater than that of glucose.

S. M.

**XXII.—Studies in Cobaltous Oxide.** By T. S. SURATEKAR, B. Sc., Royal Institute of Science.

(A) It has been shown that cobaltous oxide can be prepared by heating the cobalt carbonate under vacuum to  $670^\circ$  but the oxide obtained at higher temperatures shows a tendency to dissociate. On exposure to air the oxides adsorb oxygen and darken in colour. They contain active oxygen whose quantity decreases as the temperature of the preparation is raised. The colour of the oxide changes from yellow to brown, its density increases and the catalytic activity decreases as the

temperature of the preparation is raised but the solubility in sulphuric and hydrochloric acids is not much affected.

If the oxide is heated at a particular temperature for a long time then it does not show any tendency to dissociate and the composition of the oxide approximates more and more to the formula  $\text{CoO}$ . The stability of the oxide also increases on increasing the duration of heating, so much so that the sample of the oxide obtained at  $900^\circ$  does not change even on keeping for two months. Also the density, the solubility in sulphuric acid and the catalytic activity for the decomposition of hydrogen peroxide decrease considerably on increasing the duration of heating.

(B) The action of sulphuric acid on the mixtures of the cobaltous and copper oxides and the mixed oxides obtained on heating the mixtures of the cobalt and copper carbonates has been studied. The results obtained have been explained on the assumption that the mixed oxide is a mixture of copper and cobalt oxides when the mixed carbonates are heated up to  $700^\circ$  but the samples obtained at higher temperatures may contain  $\text{Cu}_2\text{O}$ ,  $\text{Co}_2\text{O}_3$  and  $\text{CoO}$ . The study of the systems  $\text{CuSO}_4 - \text{CoSO}_4 - \text{H}_2\text{O}$  and  $\text{CuSO}_4 - \text{NiSO}_4 - \text{H}_2\text{O}$

has indicated that no compound formation between copper and cobalt sulphates and copper and nickel sulphates takes place.

S. M.

XXIII — *X-ray investigation of the crystals of Hydrazobenzene and Diphenyl Nitrosoamine.*  
By S. G. KHUBCHANDANI.

The crystals of hydrazobenzene ( $\text{C}_6\text{H}_5\text{NHNH}\text{C}_6\text{H}_5$ ) and of diphenyl nitrosoamine [ $\text{C}_6\text{H}_5\text{N}(\text{NO})\text{C}_6\text{H}_5$ ] have been studied by the rotating crystal method using a Shearer gas tube fitted with a copper anticathode and a Bernal's Universal Photo-goniometer. The dimensions of the unit cell of the crystals of hydrazobenzene are found to be the following :  
 $a = 10.46 \text{ \AA}^0$ ;  $b = 10.60 \text{ \AA}^0$ ;  $c = 18.63 \text{ \AA}^0$

The planes (001), (010) and (100) are halved and also (0kl) are halved when  $(k+1)$  is odd, (h0l) halved when  $(h+1)$  is odd and (hkl) halved when  $(h+k)$  is odd. The crystals belong to the space group  $\text{Qh}^2$  and the unit cell contains eight molecules.

The dimensions of the unit cell of the crystals of diphenyl nitrosoamine are found to be the following :

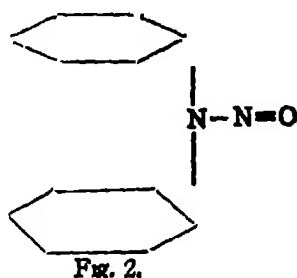
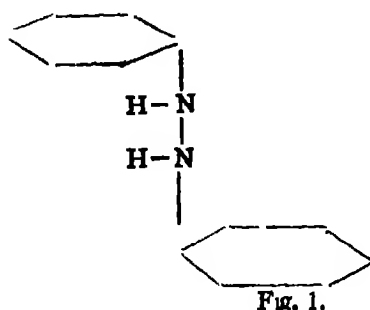
$a = 17.08 \text{ \AA}^0$ ,  $b = 8.867 \text{ \AA}^0$ ,  $c = 28.07 \text{ \AA}^0$ .

The planes (001) are quartered and (100) and (010) are halved and planes (hkl) are halved when  $(h+1)$  is odd. The crystals belong to the space group  $\text{C}_{2h}^2$  and that the unit cell contains sixteen molecules.

It has been shown that the molecules of hydrazobenzene lie as in Fig. 1. The two rings of the molecule are inclined oppositely to the face by probably  $29^\circ$ . The

unit cell of diphenyl nitrosoamine behaves like an orthogonal cell and

the molecules in the cell are placed as in Fig. 2.

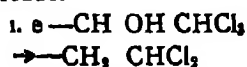


M P

XXV.—*Study of the constitution of the reduction products of chloral and bromal amides*

Part I By B H YELBURGI

Chloral amides were reduced with zinc dust and glacial acetic acid by Meldrum and Alimchandani (J. Indian Chem. Soc. 1925, 2, 1, 1929, 6, 253) and also by other workers in conjunction with Meldrum. They assigned the saturated formula to the reduction product



In the present work with chloral and bromal amides, it is found that the constitution is not as given before but of unsaturated compounds like  $\text{CH} \cdot \text{CCl}_2$  or  $-\text{CH} \cdot \text{CBr}_2$ . The reduction products of chloral acetamide, chloral propionamide, chloral benzamide, and bromal benzamide are studied in detail. The following reactions are tried to confirm the constitution.

Action of dry hydrogen chloride or hydrogen bromide in dry etheral solution did not give the compound of closed chain as was ex-

pected but a compound of the type  $\text{CHX} + \text{CHX}_2$  (where X is halogen) is obtained which is very easily hydrolysed to  $\text{CHOH} \cdot \text{CHX}_2$ .

The presence of OH group in the compound of the type  $\text{CH} \cdot \text{OH} \cdot \text{CHX}_2$  is confirmed by the action of (1) phosphorus pentachloride (2) phosphorus pentabromide (3) acetic anhydride (4) phosphorus pentoxide (5) benzoyl chloride (6) phenyl hydrozine and (7) dimethyl sulphate.

(1) With phosphorus pentachloride the compound obtained is identical with that obtained by the action of dry hydrogen chloride on the reduction product, and it is turned into an anilino derivative.

(2) Phosphorus pentabromide gives similar products.

(3) The reaction of acetic anhydride varies with the conditions of the reaction e.g., (i) In the presence of concentrated sulphuric acid at  $0^\circ$  acetyl derivative is obtained, (ii) in the presence of concentrated sulphuric acid but at the temperature of boiling water,

original reduction product is obtained and (iii) in the presence of alkali at  $0^{\circ}$  an anhydro derivative is formed by the elimination of water from two molecules of the compound.

(4) Phosphorus pentoxide gives original reduction product.

(5) Benzoyl chloride in the presence of pyridine gives two products (i) in the warm, anhydro compound is obtained, while (ii) at  $0^{\circ}$  only benzoyl derivative is obtained.

(6) Phenyl hydrazine gives diphenylhydrazones.

(7) Dimethyl sulphate gives methyl ethers.

Other reactions like that of concentrated nitric acid, ammonia, caustic soda are also tried with benzamide compound, with a view to isolate the derivative of the other half but without success, and only derivatives of benzoic acid could be isolated.

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#### PART II.—*Condensation of bromal hydrate with aliphatic amides.*

The bromal derivatives are prepared from formamide to pelargon amide and their properties with the corresponding chloral derivatives are compared. It is found that in the case of bromal derivatives, higher homologues can be more easily prepared than the lower ones.

The following reactions of hydroxy group are studied.

(1) Acetic anhydride gives an acetyl derivative as well as an anhydro compound.

(2) Benzoyl chloride gives benzoyl derivatives.

(3) Dimethyl sulphate gives methyl ethers.

(4) Phosphorus pentachloride gives different products according to the quantities of the reagent used when the condensation product and phosphorus pentachloride are in the proportion 1:1, OH group only is replaced by chlorine atom, with 1:2 a compound with two atoms of chlorine is obtained, probably due to a tautomeric change first taking place at the CO group, while with more pentachloride the bromine atoms are replaced one by one except the last one.

Reduction of the condensation product with zinc dust and glacial acetic acid gives unsaturated compounds of the type  $R \cdot CONH \cdot CH \cdot CH \cdot Br$ , but if the reduction of the acetyl derivative of the condensation product is carried out under similar conditions, the reduction products have the constitution similar to chloral derivatives i.e.  $R \cdot CO \cdot NH \cdot CH \cdot C \cdot X_2$ .

G. V. J.

#### XXVI.—*Condensation of alkyl-o-toluidines with chloral hydrate.* Part I—By A. H. ADVANI for the M. Sc. degree in March, 1933.

Methyl and ethyl-o-toluidines are condensed with chloral hydrate in the presence of fused zinc chloride and the condensation products were isolated from the hydrochloride by means of am-

monia. They are converted into nitrosoderivatives by means of nitrous acid and their mono and di-acetyl derivatives are described. These acetyl derivatives give the same reduction product *p*-( $\beta$ -dichloroethylene)-O-N-alkyl-acetotoluidide when reduced with zinc dust and glacial acetic acid. The condensation product with dilute sulphuric acid forms sulphate.

The diacetyl derivative on oxidation with potassium permanganate gives acid which on deacetylation gives *p*-methylamino-*m*-toluic acid which proves the point of attack for chloral hydrate.

**PART II.—Nitration of chloral alkyl-*o*-toluidines and chloral alkylanilines**

By the action of concentrated nitric acid, at the temperature of freezing mixture, on *p*-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl) O-methyl toluidine I a mono-nitro compound II, with the nitro group in O-position to the amino group and chloral group intact is obtained. The diacetyl derivative of II is described. If the mono or diacetyl derivatives of I are nitrated, 2-methyl-4-( $\alpha$ -hydroxy  $\beta$ -trichloroethyl) phenyl N-methyl nitramine III is obtained which is acetylated.

With warm nitric acid, I gives a dinitro compound IV with the other nitro group in place of the hydrogen of the amino group. This is further acetylated. Still further action of nitric acid removes the chloral group and it is replaced by a nitro group. This nitro compound with concentrated sulphuric acid gives a dinitronitroso

amine.

When compound IV is oxidised with alkaline potassium permanganate 4-methyl nitramino-3-methyl-5-nitro benzoic acid is obtained.

Similar compounds are obtained from *p*-( $\alpha$ -hydroxy  $\beta$ -trichloroethyl)-O-ethyl toluidine.

From *p*-( $\alpha$ -hydroxy- $\beta$ -trichloroethyl) dimethyl aniline, a trinitro compound is obtained with chloral chain unaffected and a hydrogenation of the dimethyl amino group replaced by nitro group, but by further action, whole methyl group is replaced by nitro group. Their acetyl derivatives are described.

**PART III—Halogenation of chloral-Alkyl-*o*-toluidines and nitration of the resulting products**

Bromination and chlorination of chloral methyl and ethyl-*o*-toluidines is carried both in the presence and absence of a carrier (Iodine), when mono-halogen derivatives are obtained in both cases, with halogens in O-position to the amino group. This is proved by preparing di-acetyl derivatives and by oxidising with alkaline potassium permanganate when a bromo or chloro ketonic acid is obtained.

With nitric acid, these halogen compounds give nitroderivatives with nitro group in place of the hydrogen of the amino group as proved by the formation of only monoacetyl derivatives.

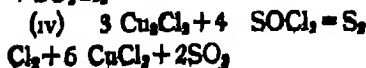
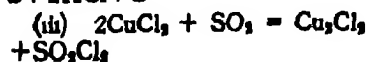
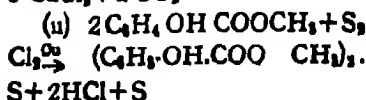
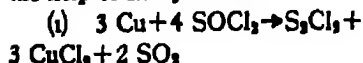
G. V. J.

**XXVII.**—*"Interaction of thionyl-chloride with the esters of Aromatic Hydroxy acids in the presence of finely divided copper"* (A synthesis of thioethers of the aromatic hydroxy acids). By Y. M. CHAKRADEO, the Royal Institute of Science, Bombay.

Thionyl chloride is known to react with aromatic hydroxy compounds, producing chloro-derivatives, esters of sulphurous acids, Sulphoxides or Sulphones depending upon the conditions of reaction.

Phenols react vigorously with thionyl chloride to give condensation product, containing sulphur, while acids, including hydroxy benzoic acids, yield acid chlorides or anhydro compounds, wherever they react. It was, therefore, of interest to see if hydroxy benzoic acids could be made to give these compounds. Esters of hydroxy acids in question were used since it was found in this laboratory (by N. W. H.) that various anhydro compounds are formed by the interaction of  $-OH$  and  $-COOH$  groups.

The mechanism of the reaction can be illustrated as follows, with the help of salicylic acid.



Thionyl chloride first reacts with copper to give sulphur monochloride, which in its turn, acts, in presence of Copper, on the ester to yield the condensation product. Copper chloride is formed in the first stage and sulphur precipitated during the second part of the reaction. Sulphur dioxide, which is abundantly formed in the reaction reduces cupric chloride to cuprous chloride, which is acted by thionyl chloride again to produce more of sulphur monochloride, thus rendering the reaction continuous.

Following reactions lead their support to the proposed mechanism.

(a) Anhydrous cuprous chloride in place of finely divided copper reacts to give the condensation product.

(b) Hydrated cupric chloride reacts to give the product, but anhydrous cupric chloride does not react to give the product. It reacts to give the product only when a trace of water is added or sulphur dioxide is passed in the reaction mixture.

(c) Sulphur monochloride alone does not react so as to produce the thio ether, which is easily obtained in presence of small quantities of copper.

As regards the constitution of the condensation product (a) the presence of the  $-OH$  group in the molecule has been proved by preparing acetyl, benzoyl and methoxy derivatives; (b) The sulphur linking in  $p$ -position to the  $-OH$  group has been confirmed by denitrating the cop-

densation product; (2) by brominating it first and then nitrating the bromo compound and thus getting the known bromo-nitro derivatives. When the compound is heated above  $280^{\circ}$ , hydrogen sulphide is evolved, showing the presence of the sulphide structure.

Thus the thio-ethers of salicylic acid, O- and M-cresotinic acids and 4-methoxy salicylic acid, have been prepared with their various derivatives and salts.

N. W. H.

**XXVIII.—Derivatives of salicylic acid** by M. R. Jambhakar (The Royal Institute of Science, Bombay).

The Thesis is divided into three parts —(1) Study of the isomeric nitro-toluene-sulphonic acids (2) synthesis and constitution of 4-sulpho-salicylic acid (3) Derivatives of 4-sulpho-salicylic acid.

PART I.—Nitration of toluene p-sulphonic acid is effected so as to get the sulpho-nitro-toluene free directly, using acetic anhydride in the place of concentrated sulphuric acid as a medium for nitration.

O-nitro-toluene also has been sulphonated at various temperatures with the view to find out whether 2-Nitro-toluene-6-sulphonic acid is obtained together with the 2-nitro-toluene-4-sulphonic acid. The work is in progress and it is expected that 2-nitro-toluene-6-sulphonic acid may be obtained from the mother-liquor on closer investigation of it.

In the meanwhile 2-nitro-toluene 6-sulphonic acid has been obtained from 2,4-dinitro-toluene-6-sulphonic acid by the elimination of the 4-nitro group. Composition of the 2-nitro-toluene-6-sulphonic acid is  $C_7H_5O_6NS$ ,  $2H_2O$ . Barium salt  $(C_7H_4O_6NS)_2$ , Ba,  $8H_2O$ . Its sulphonyl chloride is a liquid and sulphonamide m.p. ?

2,4-Dinitro-toluene-6-sulphonic acid is very conveniently obtained by sulphonation first of p-nitro-toluene and subsequent nitration of 4-nitro-toluene-6-sulphonic acid. Free-sulphonic acid can be obtained direct from the nitration mixture by slight dilution. Composition.  $C_7H_5O_7N_2S$ ,  $2H_2O$ ; Potassium salt  $C_7H_4O_7N_2SK$ ,  $2H_2O$ , sodium salt  $C_7H_4O_7N_2SNa$ , calcium salt  $(C_7H_4O_7N_2S)_2Ca$ ,  $4H_2O$ , Barium salt  $(C_7H_4O_7N_2S)_2Ba$ ,  $4H_2O$ . Sulphonyl chloride  $C_7H_4O_6N_2SCl$  m.p.  $107^{\circ}$ . Sulphonamide cannot be obtained. 2-Nitro-4-aminotoluene-6-sulphonic acid  $C_7H_5O_6N_2S$ , Potassium salt  $C_7H_4O_6N_2S$ , K,  $2H_2O$  sulphonyl chloride and sulphonamide. 4-diazo-6-nitro-toluene 2-sulphonate decomposes violently at  $160^{\circ}$ .

PART II.—On oxidation of 2-nitro-toluene-4-sulphonic acid with potassium permanganate at room temperature 2-nitro-4-sulphobenzoic acid  $C_7H_5O_6NS$ ,  $2\frac{1}{2}H_2O$  is obtained. Acid potassium salt is anhydrous, barium salt  $C_7H_4O_6N_2SBa$ ,  $2H_2O$ . Acid dichloride is liquid and diamide melts at  $223^{\circ}$ .  $225^{\circ}$  acid monochloride m.p.  $202^{\circ}$  and monoamide  $192^{\circ}$ .

On reducing the 2-nitro-4-sul-

pho-benzoic acid with tin and hydrochloric acid 4-sulpho-anthranilic acid is obtained comp— $C_7H_7O_4NS$ ,  $H_2O$ , barium salt  $C_7H_6O_4NSBa$ , 4-sulpho-anthranilamide  $C_7H_7O_4N_2S$  m. p.  $227^\circ-28^\circ$ . The diazo sulphonate  $C_6H_5N \cdot N\text{---COOH} \text{SO}_3H$ ,  $H_2O$

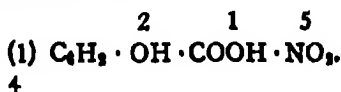
decomposes at  $163^\circ-164^\circ$ . On boiling the diazo-sulphonate with water apart from the diazo mixture free-4-sulpho-salicylic acid is directly obtained. It is hygroscopic at  $35^\circ$  (room temperature), comp.  $C_7H_6O_4S$ ,  $3H_2O$  (air dry m. p.  $82^\circ$ );  $C_7H_6O_4S$ ,  $2H_2O$  (desiccated: m. p.  $133^\circ$ ), acid sodium salt  $C_7H_5O_4SNa$ ,  $2H_2O$  Acid-potassium salt  $C_7H_5O_4SK$  Barium salt  $C_7H_4O_4SBa$ ,  $4H_2O$ : calcium salt  $C_7H_4O_4SCa$ ,  $6H_2O$ .

On fusion with potassium hydroxide 4-sulpho-salicylic acid gives 2,4 dihydroxy benzoic acid ( $\beta$ -resorcylic acid) m. p.  $208^\circ$ .

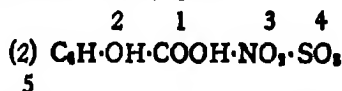
PART III.—4-sulpho-salicylic acid is nitrated, and brominated and it has been shown that not only mono-nitro-sulpho and mono-bromo-sulpho-salicylic acid is obtained, but a dinitro-sulpho and a dibromo-sulpho-salicylic is obtained: which shows the unusual stability of 4-sulphonic acid group; unseen in 3-sulpho and 5-sulpho salicylic acids. Tribromo-4-sulpho-salicylic acid also is obtained on

further bromination which shows that the directing influences of  $p\text{---}Br + m\text{---}SO_3H + O\text{---}Br$  than the repelling influences of  $\text{---}OH$  or  $\text{---}COOH$ .

The compounds described are as follows.—

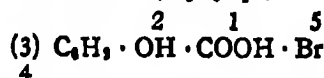


$SO_3H \cdot 2H_2O$ , m. p.  $166-167^\circ$ . Potassium salt,  $C_7H_4O_4NSK$ ,  $H_2O$ : barium salt  $C_7H_3O_4NSBa$ ,  $H_2O$ : amino acid  $C_7H_7O_4NS$ .

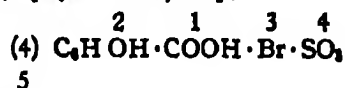


$H \cdot NO_2$  (decomposes above  $260^\circ$ ).

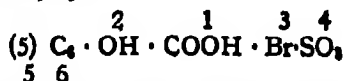
Potassium salt  $C_7H_5O_{10}N_2SK$ , barium salt  $C_7H_4O_{10}N_2SBa$ ,  $2H_2O$  mono-amino acid  $C_7H_6O_4N_2S$ : diamino acid— $C_7H_5O_4N_2S$ .



$SO_3H$ ,  $3H_2O$ —Acid potassium salt  $C_7H_4O_4SBrK$  barium salt  $C_7H_3O_4SBrBa$ ,  $4H_2O$ .



$HBr$ ,  $H_2O$  barium salt  $C_7H_3O_4SBr_2Ba$ ,  $4H_2O$ .



$H \cdot Br \cdot Br \cdot 4H_2O$ . barium salt  $C_7HO_4SBr_2 \cdot 2H_2O$ .

N.W.H.



## Notes and News

We are glad to note that our "Notes and News" in the issue of last September were reviewed in the 1933 February Number of the *Nature* (No. 3303, Vol. 131) and the main idea underlying them was favourably endorsed by its editor. We pointed out then that there was a serious gap between the rapid scientific advance on the one hand and the stationary ethical position on the other—a gap which threatened the disruption of civilisation and that it was the urgent duty of every university to see that this gap was closed up, that the advance of science proceeded along a parallel advance in man's ethical and spiritual development, and that the motto of science should be not only Truth but Truth and Service.

The failure of the World Economic Conference recently held in London from which large developments were expected and on which great hopes were built is one more illustration of the statement made above. The cause of the failure of the Conference may be summed up in one word. The statesmen of the different countries of the world who met together for the first time in the history of the world for evolving a common formula to solve the present day economic world problem did not agree for the simple reason that they did not think in terms of humanity as a whole and did not wish to plan for the whole of mankind but each representative thought in terms of his own country and wanted to get as much for his country as possible. A very narrow outlook indeed! It seems that the following lesson has not yet been learnt, *viz.*, that the world is one organic whole and that the different countries of the world are so many parts of that organism and that one country cannot expect to prosper at the cost of another country, however small it may be; all rise and fall together. The weakness of one part of the human organism makes the whole organism weak. Each one should co-operate with and help the other if the whole organism is to be made sound and healthy. If the present world depression has not taught this lesson then what will? If the last great war, with all its direful after-effects, has not taught this lesson then what will? Are still greater suffering and misery and economic depression necessary to teach that lesson? Suffering is the greatest of teachers. But is there no other alternative? Cannot the same lesson be learnt in some other way

without undergoing suffering? Yes, it is possible. *A new orientation is necessary.* In giving this new orientation the university could and should play a very important part. If it is taught from the very beginning that there is a greater pleasure and happiness in giving and sharing what one has got with others than in receiving then the knotty economic problems will automatically disappear. This brings us once again to the question with which we began *viz.*, how to bridge the great gulf between the rapid scientific and engineering advance on the one hand and the stationary ethical position on the other? How to make man control himself before the control of Nature is put into his hands? In other words, how to make him ethically fit to enjoy the gifts of science? How to make him realise his great responsibility as to the use of the forces of nature placed under his command? If he makes a good use of them then peace and joy, plenty and prosperity, leisure, culture and refinement will be the blessings he will be able to give to the whole humanity. On the other hand, if he made a bad use of them then the whole fabric of civilisation would tumble down. These dangers to our present civilisation, due to the neglect of the ethical values, have been recently emphasised by the distinguished Presidents of the British Association, Sir Alfred Ewing and General Smuts.

The excellent and thoughtful lecture given by Dr Alexander Findlay, on "Science and the Community" on 10th November 1932 at the Textile Institute, Manchester, strikes the same note and deserves our careful study. This lecture is an attempt to show that in the study of science the utilitarian point of view has been too much emphasised at the cost of the development of the finer qualities of human nature. In the study of science we should see that the human factor and the higher values of life are not lost sight of. *Science* should now be *humanised*. The *cultural* and *spiritual* side of *science* should now be *emphasised*. Dr. Findlay wants the Scientists to recognise that Truth which is the Motto of Science is only one of the three great primary aims or ends in human nature; the other two are Beauty and Goodness which are equally important. If we desire human nature to be developed fully and completely, if we wish to have an all round development of the human personality then all these three aims must be pursued. There is no sharp line of demarcation between Truth, Beauty and Goodness. Some branches of study emphasise one aspect and some another but each of the following subjects given in the table below should be treated in such a way that while it emphasises one aspect it should not neglect the other two:

Truth, Beauty, Goodness	}	(Mathematics, Science, Philosophy)
Truth, Love, Service		
Truth, Beauty, Goodness	}	(Aesthetics, Art, Literature)
Truth, Love, Service		
Truth, Beauty, Goodness	}	(Civics, Ethics, Humanitarianism)
Truth, Love, Service		

There is no religion higher than **Truth**.

There is no power greater than **Love**.

There is no duty nobler than **Service**.

We thus see that truth satisfies the claims of the intellect, beauty satisfies the claims of emotions and goodness satisfies the claims of what is the highest and the noblest in man (*viz.*, Spirit) which finds expression in the *will* to be true, loving and serviceable. These three should constitute the **Religion of Humanity**. It is this religion which the University and the State should inculcate in its alumni and its people—a religion of **Truth, Beauty and Goodness**,—a religion of **Truth, Love and Service**. It should, therefore, be the main function of the University to see that it provides such facilities to its students and it should be the duty of the Government and the leaders of the people to see that they bring about such an order of society that human nature may be able to find its fullest and most complete expression through the cultivation not only of "truth" but also of "beauty" and "goodness," of love and service.

In light of what we have said above if we examine what is being done by our University to satisfy the three great primary ends in human nature we cannot help feeling intense disappointment. In our University only one aspect is emphasised *viz.*, that which satisfies the claims of the intellect and that, too, not sufficiently strongly and except for the study of literature the two other aspects are ignored altogether. It is very necessary that steps should be taken to introduce, one after another, courses of study which would make up for the existing deficiencies and help to create a new generation of men and women with an altered mental outlook who would be *true* to themselves and *loving* and *helpful* to others.

D. D. K.

We take this opportunity of offering our congratulations to Sir Chandrasekhara Venkata Raman Kt. on his being the first Indian Director of the Indian Institute of Science, Bangalore. A Fellow of the Royal Society, England, a Nobel Laureate in Physics and a great scientist of international reputation, Sir C. V. Raman will prove to be a capable Director and being a researcher of first rank himself will infuse his spirit of research into one and all working there. Having set a noble example of sacrifice at an early age by giving up a lucrative post in the Finance Department where he would have risen to the highest grade he devoted himself to research and became a true votary of Sarasvati. A man of such high attainments and noble character is bound to inspire all the workers at the Institute, both teachers and students alike, and we have every hope that under his leadership the Indian Institute of Science will fulfil the destiny which its princely donor, the late Mr. Jamshedji Nassarwanji Tata, had contemplated for it.

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Living as we do in the twentieth century—a century in which science has made such rapid progress in different directions—it becomes increasingly clear that the nation which is the first to take advantage of the applications of science, be it in matters of food and nutrition, or industry and commerce, or agriculture and medicine, or sanitation and hygiene will remain in the vanguard of civilization and its people will become the leaders of the race. Knowing this as we do we note with regret that Ahmedabad which boasts of being the Manchester of India has not got a single Central Laboratory where raw materials could be analysed and where researches on a number of problems connected with the textile industry could be carried out. There are more than 80 textile mills in Ahmedabad which buy thousands of tons of raw materials every year for their different departments which in money value come to about two crores of rupees. The address\* given by Dr. T. S. Wheeler on the applications of Science in the Textile Industry shows in how many different directions science would be helpful in the mill industry.

Contrast with this sad spectacle the picture presented by Messrs. Lyons & Co. of England who are mere caterers but who were enlightened enough to recognise and appreciate the value of science in their own business. They began with one small laboratory and one chemist in 1919; within six months they found that one chemist was not enough and they added another; in 1927 they had 77 well-trained, handsomely paid chemists working either in the analytical or research section of a

\*The address on "The Applications of Science in the Textile Industry" was given by Dr. T. S. Wheeler, Principal, Royal Institute of Science, Bombay on 3rd December 1932 on the occasion of the Thirteenth Annual Social Gathering of the Gujarat College Scientific Association, Ahmedabad. A copy of this address will be obtained free of charge from Prof. D. D. Kanga, Gujarat College, Ahmedabad.

big laboratory. This is an excellent illustration of the fact that the applications of science and the employment of scientists in an industry are capable of increasing the dividends in that industry and bringing prosperity to it. When will *our* industrialists realise this ?

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A person cannot live without air for more than three minutes, without water for more than three days and without food for more than three months. This shows the relative importance of air, water and food. With regard to air and food attention is invited to the two articles in the present number, one on 'Smoke and its prevention' and the other on 'Dietetics Food and Race'

It is not an unusual sight to observe in a big industrial city like Ahmedabad every evening in cold weather more than a hundred tall chimneys belching forth smoke and polluting the atmosphere. The more polluted the atmosphere of the place by smoke and dust, the greater the number of people suffering and dying from respiratory diseases. Smoke nuisance is due to (1) factory smoke, (2) domestic smoke, (3) dust, and (4) calm still atmosphere in winter. The total quantity of coal consumed in factories and mills in a city like Ahmedabad is about 1500 tons per day. The smoke in the atmosphere indicates so much coal wasted and so much energy lost. What is the remedy ? The article on 'Smoke and its Prevention' shows the lines on which the industrialists using large quantities of coal should proceed if they wish to tackle this problem, the adoption of the measures given therein would, not only, help the industrialists to effect a great deal of saving on their fuel bills, but also help to improve the sanitation of the city by keeping the atmosphere pure and unpolluted as far as possible.

One of the measures to reduce the nuisance due to domestic smoke, particularly in the area inhabited by the labouring population which number more than a third of the whole population in a city like Ahmedabad, is suggested in the article 'Dietetics Food and Race'. The author discusses in this article the intimate relationship between health, physical efficiency, and output of work of the working population on the one hand and the food they eat on the other. It necessarily follows therefrom that if the industrialists wish to have an increased output of work they will have to pay more and more attention to the food of their workers. Again, the preparation of a well-balanced diet presupposes a fair knowledge of the foodstuffs, which one cannot expect our labourers to possess, it would, therefore, be to the advantage of the industrialists if they provided properly constituted meals to their workers in big halls specially provided for the purpose as is being done in Japan. The meals would be prepared in about a dozen big kitchens each catering for its own class of people and using only *smokeless fuel* (soft coke). This is purely a business

proposition and we cannot too strongly impress upon the industrialists of big cities like Calcutta, Bombay, Ahmedabad, Nagpur, Cawnpore etc., of our country the need of paying their serious consideration to this important question. The example of Japan is before them. One of the reasons of the greater efficiency, and consequently the greater output of work by their workers, is the meticulous care the Japanese take in providing them with properly constituted meals under the supervision of doctors. If our industrialists properly tackle this problem they will not only benefit themselves by having an increased output of work but will also have the satisfaction of improving the sanitation of the city and the health of the people by diminishing the nuisance due to household smoke.

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Millions of people in India live on a purely vegetarian diet. The researches carried out on nutrition have shown what a great influence a well-balanced diet has on the health, physical efficiency, powers of endurance, freedom from diseases, output of work etc., of those taking such a diet. They have again shown that it is necessary to have a certain proportion of animal protein and animal fat in the food of every person. Major-General Sir Robert McCarrison has calculated that to be 33% animal protein and 50% animal fat. The only food materials from which the vegetarians could expect to get these nutritious constituents are milk and milk products like curd and butter. It is therefore of the utmost importance that these should be available in a pure and unadulterated form.

The large number of raids and prosecutions that we had of late in Bombay in connection with butter and the large number of facts which have come to light in that connection show that the adulteration of food-stuffs, particularly of ghee and butter and also of milk is going on at a rate and on a scale which are simply scandalous. The existing law is not strong enough to act as a deterrent on the miscreants. It is therefore absolutely necessary that a new act should be passed which would permit of the imposition of not only a very heavy fine on those found manufacturing and (or) selling adulterated food-stuffs which are vital for the health of the people but also rigorous imprisonment.

The laws of a country reflect the progress and civilization of its people. If Mother-India wishes to have a nation of healthy, strong and virile sons and daughters, then she must see that her children get pure air to breathe, pure water to drink, pure and wholesome food to eat and clean and healthy surroundings to live in. She should, therefore, see that she has got adequate laws to punish those who pollute the atmosphere, contaminate the water and adulterate the food materials.

D. D. K.

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## INDIAN SCIENCE CONGRESS

In February last, representatives of various scientific and educational institutions in Poona met together and decided to invite the Indian Science Congress to hold its 21st Annual Session in Poona in January 1934, under the auspices of the University of Bombay. The university also agreed to this proposal and sanctioned a grant of Rs 2000 towards the funds of the Local Executive Committee, who took up arrangements in connection with the Session. The Vice-Chancellor, Mr V N. Chandavarkar was elected Chairman of the Local Executive Committee and the Director of Public Instruction Mr. R. H. Beckett the Vice-Chairman, and representatives of the local scientific, educational and civic institutions were the members. They were assisted by two Honorary Secretaries Mr V. V. Sohoni of Meteorological Office, Poona, and Dr D D Karve of Fergusson College.

After carrying on preliminary work of organising the meeting and collecting quite a considerable amount of money, the continued prevalence of plague in an epidemic form made it necessary to change the venue of the Congress to Bombay. Major Bhatia, the Dean of the Grant Medical College and Prof P R. Awati of the Royal Institute of Science were appointed as additional local secretaries and they took up the work of organising the meeting with the co-operation of the old local secretaries as well as of the Staff of the Royal Institute of Science. The session was a great success from every point of view and the attendance of members from other provinces was entirely satisfactory. A handbook of information of Bombay and Poona containing contributions from a number of authorities on different aspects of educational and scientific activities was published to commemorate the occasion and will prove a valuable book of reference. The address of the President of the Congress, Prof Megh Nad Saha, of the sectional presidents, the popular evening lectures and the social entertainments were all greatly appreciated by the delegates and the conference has been of great value in promoting scientific interest in our presidency.

D. D. K.

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## THE EIGHTH CONFERENCE OF THE INDIAN MATHEMATICAL SOCIETY, JUBILEE SESSION

At the invitation of the University of Bombay, the Indian Mathematical Society held its eighth Conference in Bombay from the 21st to the 24th December 1932. It was presided over by Rao Bahadur P. V. Seshu Aiyar I E S. (Retired) and a member of distinguished mathematicians including Dr. Megh Nad Saha, Mr. V. Ramaswamy Iyer, the founder of the Society, Mr. M. T. Naranengar, Principal A. V. K.

# THE INDIAN MATHEMATICAL SOCIETY.

EIGHTH CONFERENCE, SILVER JUBILEE SESSION, BOMBAY.

22ND DECEMBER 1932.

TOP ROW —Messrs. M. V. Divatia, A. D. Lawrence, B. V. Patil, S. H. Bhat, P. S. Paralkar, C. M. Fakh, S. S. Kavalakar,  
S. S. Ghadiali, E. R. Shah, K. R. Goshkar, G. R. Paranjpe, D. P. Patravall, C. J. Shah, A. R. Rao,  
J. R. Rane, L. H. Marathe

2ND ROW —Messrs. P. V. Dandekar, N. D. Doctor, S. P. Khanna, A. L. Shaikh, V. A. Pandit, B. B. Bagel, R. Rajad,  
K. Naghibhawanam, G. V. Bhagvat, A. R. Sayed, K. N. Wani, C. R. Chaturvedi, P. K. Keshkar,  
S. R. Shaikh, M. V. Pandit

3RD ROW —Messrs. D. D. Vaidya, P. N. Sakeshwala, R. Vaidyanathswamy, L. S. Vaidyanathan, J. N. Dharap, D. M. Patel,  
B. S. Kulkarni, F. H. Gracia, C. N. Srinivas Lingar, B. S. Madhav Rao, S. Sastry, I. Mathai,  
G. S. Mahajani, K. M. Shah, G. L. Chandratreya.

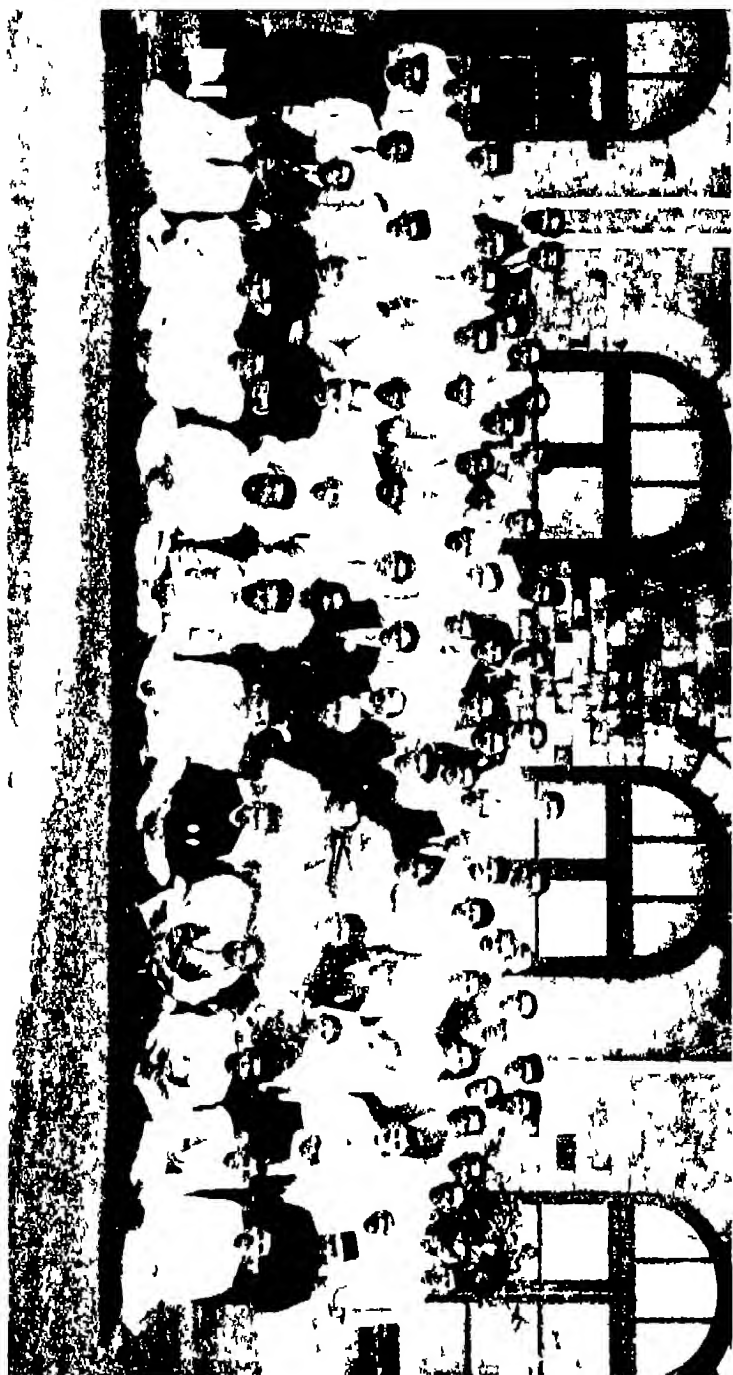
BEHIND CHAIRS —Poon, Messrs. B. K. Wagle, K. C. Shah, M. K. Kevakramani, A. K. Krishnaswamy Lingar, K. D. Pandey,  
S. S. Pillay, D. M. Mehta, S. M. Shah, R. Siddiqui, K. S. K. Lingar, T. Buell, N. M. Shah, T. S. Wheeler,  
B. G. Nadkarni.

CHAIRS —Messrs. Ram Behari, M. V. ARANACHALA SHASTRI, D. D. KAPADIA, M. T. NARANIENGAR, A. V. K. MENON,  
P. V. SESHU AIYAR (President), V. N. CHANDAVARKAR (Vice-President), V. RAMASWAMY AIYAR,  
Mrs. Seshaswamyam, Messrs. V. B. Nalk, S. B. Belkar

GROUND —Messrs. D. N. Patankar, S. K. Abhyankar, P. K. Oke, S. V. Pimpalekar, M. L. Chandratreya, G. R. Deo,  
C. A. Sheth, C. K. Koshi, K. V. Iyengar, B. S. Gai, N. H. Phadke.









Menon, Prof. Arunachala Shastri and others attended the Session. Dr. Megh Nad Saha F.R.S. gave a public address on "The Present Crisis in the Science of Dynamics". The session was also the occasion for the celebration of the Silver Jubilee of the Society.

H. E. Sir Frederick Sykes, the Governor of Bombay and the Chancellor of the University was the Patron of the Conference and gave an inspiring Inaugural Address on the morning of the 21st December. Mr. V. N. Chandavarkar, our present Vice-Chancellor then Mayor of Bombay, took a keen interest in the Conference as the Vice-Patron and he and Mrs. Chandavarkar were "At Home" to the conference on the evening of the 23rd December. Principal John McKenzie, then Vice-chancellor, was the chairman of the Reception Committee and presided at the public address by Rao Bahadur P. V. Seshu Aiyar on "The Nature of Mathematics and Religion" on the 24th December, that being also the occasion for the celebration of the Silver Jubilee of the Society.

Principal N M Shah, Principal G S. Mahajan and Prof. K. R. Gunjkar were the delegates from the University of Bombay to the Conference. Prof G. R. Paranjpe, Mr. D C. Pavate and Prof. K. R. Gunjkar were appointed by the Board of Studies in Mathematics to be in charge of the local arrangements, Prof. Gunjkar being the Honorary Local Secretary.

An interesting programme was carried out which besides the reading and discussion of papers included three public addresses (in addition to those by Dr. Saha and Rao Bahadur Seshu Aiyar, one by Dr. R. Vaidyanath Swamy on the "Nature of the Continuum"), two "At Homes", (one with Mr. and Mrs. Chandavarkar and the other with the Reception Committee), Jubilee Celebration and presentation of an address to Mr. M. T. Naranengar (a visit to the Oriental Life Assurance Company's offices) and a trip to Elephanta. The public functions were arranged at the Sir C. J. Public Hall, while the rest of the programme took place at the Royal Institute of Science at the kind invitation of the Principal Dr. T. S. Wheeler. As a special feature of this Conference, were the two Discussions on the teaching of Mathematics in schools and in the University which were well-attended and greatly appreciated.

The Conference ended with a trip to Elephanta on the 24th December. The expenses were met from the generous grant of Rs. 1000/- made by the University of Bombay, for which thanks are due from all interested in the progress of Mathematics in this Presidency. It is to be hoped that the enthusiasm created by the visit of the Society to Bombay will be kept alive by the foundation of a School of Mathe-

matics under the auspices of the University. The public of Bombay led by the Mayor also showed a keen appreciation of the work of the Conference by contributing handsomely to the reception of the Delegates and attending the public functions in large numbers. The Conference passed sincere votes of thanks to them all.

K. R. G.





THE FAIR RIVER SACAS

# Obituary

## The Late Rev F Sacasa, S J

On July 1, last—shortly after the re opening of the College, one of the Bombay Colleges, St Xavier's College, lost its Principal, the late Rev F Sacasa S J, who died at the early age of 44

Fr. Sacasa had been Principal of the College for a little more than a year only, but he had already won the esteem of staff and students alike by his genial manner, his constant cheerfulness and his sympathetic treatment of all alike. A large educational institution offers new and often intricate problems day by day, and the man who is called upon to solve these, has a difficult task set before him. Fr. Sacasa entered upon his work with a spirit of great optimism and after winning the sympathies of all those with whom and for whom he had to work, his task became a fairly easy one, even though at times the large amount of routine work, taxed his physical strength to its utmost. He was perhaps too anxious to do well, and the heavy work at the beginning of the new academic year told on his health.

To make matters worse, Fr. Sacasa had for some time been suffering from slight chronic appendicitis, which now became acute and an operation became necessary. In spite of his own, the Doctors' and his friends' confident hopes, the patient was not able to stand the strain of the operation and he died a few days later.

The funeral which was largely attended by students as well as by many of his colleagues, of other Colleges, showed how popular the deceased was. The University was represented at the funeral, by the Vice Chancellor himself and the Registrar. The death of one of its most able professors is a great loss to St Xavier's College. All the Bombay Colleges held condolence meetings, or closed for one day in token of respect for the memory of the deceased.

Fr. Sacasa was born at Barcelona, Spain, on June 7, 1889. After his early education in his own native town, he joined the Jesuit Order at the age of 16, and went through the ordinary course of a Jesuit education—in his case no less than 13 full years of classical, philosophical and theological studies, to which were added special studies of science and especially chemistry, which he was ultimately to make his special branch. He spent a number of these years in America, mostly at the University of St Louis, Missouri. After completing his studies of philosophy, he was sent to teach chemistry for a number of years, at



the Ateneo, the Jesuit School of Manila, in the Philippine Islands, after which he returned to the United States, where he specialized in chemistry before he came out to Bombay to take up the post of Professor of Chemistry at St. Xavier's College. Thus he held from 1924 till the end of his life, adding to it the work of Principal during the last year.

Fr. Sacasa was a man of rare talents, of quick perception, and capable of getting through a large amount of work in a short time. His scholastic career had been brilliant, and as a teacher he was able to hold the attention of his hearers and to make the teaching of a very dry subject, both lucid and interesting. He was, of course, frequently an Examiner in Chemistry, and at the time of his death he was a member of the Senate, of the Academic Council and of the Syndicate of the Bombay University.

G. P.

## Reviews

Contribution à l'analyse des substances toxiques et des stupéfiants. Sur la découverte de la non-spécificité des réactions chimiques employées pour déceler la présence du chanvre indien ou hachich et dérivés. Par Henri Trollé, Ingénieur-chimiste diplômé de l'école d'ingénieurs de Lausanne, expert français près le tribunal mixte du Caire. Le Caire—Imprimerie Paul Barbey. 1933.

This short pamphlet of 21 pages contains two parts—

1. In the first part the author describes chemical experiments which prove that (i) Beam's reaction may fail to detect the presence of cannabinol in an extract which contains it, (ii) this same reaction obtains with other drugs than Indian Hemp and is not, therefore, specific; (iii) there is no specific reaction for cannabinol.

2. The second part is a reprint of Dr Giuseppe Rende's contribution to *Officina* No. 6, November-December 1931, in which he proves by chemical and physiological experiments that Beam's reaction is not specific for Indian Hemp.

J. F. C.

*Through Wonderlands Of The Universe.* By R. K. GOLIKERE. Pp. XVIII+400 with Frontispiece. Taraporevala Sons and Co., Hornby Road, Bombay. Price Rs. 6-4-0.

This book deals with a variety of subjects of geological, physical, astronomical and astrophysical nature and in the words of the author "it is not a learned treatise, but a simple elementary study, a modest attempt to awaken a taste for Science among those who ordinarily take little interest in it".

The first chapter contains information about the nature of the earth and a collection of some interesting finds in its interior observed in different parts of the world. The chapter ends with remarks on some theories about the physical state of the earth's interior, causes and nature of earthquakes and their probable depth. In the next chapter is given some interesting information about the ocean, with a brief account of marine zoology. The third chapter contains information about some well-known low-lying lands, mountains, lakes, springs, waterfalls, heights of some clouds, structures built in various parts of

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the world, the highest heights reached by balloons, birds, men etc. It also incidentally describes the nature of work done at various offices of the India Meteorological Department. The next two chapters give information about volcanoes and detailed accounts of some well known volcanic eruptions and the giant peaks of Asia.

Chapters VI, VII, VIII and IX deal with the troposphere, the tropopause, the stratosphere and still higher regions of the earth's atmosphere. These chapters contain information about phenomena observed at various heights in different parts of the world. A short account of researches of various investigators, of some natural phenomena and of the composition of the atmosphere is also given in these chapters. About these chapters it should be stated that the author could have given a more connected account of the various causes which are responsible for the weather experienced over different parts of the world and thus create an interest about a subject which concerns everybody from the point of view of the prosperity of the country—especially of a country like India whose major part of the population lives on Agriculture

In chapters X to XVII the author has treated the subject of solar system, the galactic system and of the physical condition of stars and the nebulae. Probably the subject being too wide the author could not give much attention to various details about celestial bodies which one would have liked so much

The author describes some giant telescopes of the earth in chapter XVIII. The next three chapters are short and deal with "Outer Space", "the Roof of the Universe" and the views of Sir Arthur Eddington on "Space and the Universe". Chapter XXII gives some idea about the weight of the Universe.

The last two chapters give a brief account of Astronomy in Asia up to the 18th Century and Hindu Cosmogony and Cosmography.

In this book the author has dealt with a variety of subjects and as such it is but quite natural that too much detail about various things could not be given. The author has been very careful in his selection of things to be presented to the reader in order to make the book popular, and as far as possible, has taken note of some of the latest relevant investigations. The book is sure to awaken a taste for Science amongst laymen—this has been the aim of the author in writing this book—and the author should be congratulated on it.

B. N. D.

*The Physical Nature of the Universe.*—By J. W. N. SULLIVAN.  
Victor Gollancz Ltd. pp. 143, price 1s. 6d

It is no easy task to describe within the compass of a little more than one hundred pages the modern revolution in physical thought, but the author of this book (Outline series) has done it in an admirable manner. He begins with Galileo who is considered to be the first man to make the idea of motion precise and amenable to exact mathematical treatment. Then he gives a brief account of the dynamical theory of heat and the kinetic theory of matter. In a short chapter that follows he clearly describes the various vicissitudes through which the atom has passed, shows how the hard and unbreakable atom of old had to make room for the Rutherford-Bohr atom having an exceedingly complex structure and how even this recent model has been finally abandoned so that at present the atom has passed out of all recognition and remains merely a mathematical symbol. Then he takes up the question of the ether and shows how the conflict between the results of experiments designed to investigate its properties brought us to the restricted theory of Relativity and describes some of the important results of this theory. Next he turns to the problem of gravitation and shows how Einstein's General theory of Relativity which attributes gravitation to the curvature of space is more logical and satisfying than the old Newtonian conception. Lastly he shows how all the known laws of physics are macroscopic and therefore statistical and how Heisenberg's Principle of Indeterminacy makes exact measurement of the properties of individual atoms impossible and thus strikes at the root of the doctrine of scientific Determinism. Broadly speaking modern physics tends to think of the universe as much more subjective than the old and the methods of science cannot tell us anything about the ultimate stuff of which the world is made, at the most they give us some idea of its structure.

The book is written in a simple and nontechnical language and can easily be followed by those who have a desire to get a glimpse of the trend of modern physical thought but have neither the leisure nor the equipment to read the more ponderous treatises on the subject.

S. N. D.

*Practical Chemistry.*—By N. M. SHAH, M. Sc., Second Edition  
(Dharwar. The Students' Own Book Depot, 1933).

In this handbook the author has made a successful attempt to meet with the requirements of the syllabus of the Intermediate Science course in Practical Chemistry of the University of Bombay,

Part I deals with the methods of preparation and purification, a study of the properties of simple and compound substances, determination of equivalent and molecular weights and exercises in gravimetric and volumetric analysis commonly recommended in elementary practice.

Part II gives an account of the customary dry and wet reactions of positive and negative radicals and of the systematic procedure to be followed in the qualitative analysis of a single substance.

Special attention has been paid to emphasise the fundamental principles of theoretical chemistry and to show how a neat entry of the experimental results and calculations obtained therefrom can be made in the journal.

The book is expected to be of great use to students as well as instructors of the Intermediate Science Chemistry Classes.

M. S. S.

*The Fourier Integral and Certain of its Applications.* By Dr. N. WIENER, 1933. (Cambridge University Press)

The subject of Fourier series has been fairly exhaustively treated in a number of standard treatises on Theory of Functions and in special books on the subject. The same has not been the case with the Fourier integral and one is compelled to refer to various journals for results which would have otherwise found a natural place in a modern work on the subject. Dr. Wiener's book is in no sense a systematic treatise on the subject nor was it written from that point of view. It is an elaboration of a course of lectures delivered at Cambridge and hence in a sense, as the author himself says in the preface, the treatment is fragmentary. We welcome the book, however, as it makes available in a book form most important recent researches on the subject from the pen of an author who has himself contributed so much to the development of the subject.

For generality of results Lebesgue's theory of integration is indispensable, and in the introductory chapter the author gives a résumé of that theory as well as a short discussion of developments in orthogonal functions.

The modern theory of Fourier integral starts with Plancherel's theorem, that if

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} g(u) e^{iux} du, \quad g(u) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{+\infty} f(x) e^{-iux} dx,$$

and if  $|f(x)|^2$  is integrable ( $L$ ), then  $|g(x)|^2$  is also integrable ( $L$ ). Chapter I deals with Hermite's polynomial and Hermite's functions and the above theorem is established with their help. Chapter II deals with the General Tauberian Theorem. It is not apparent how a Tauberian theorem, which is statement of conditions under which we can pass from one limit relation to another, could have any connection with Fourier integrals. Dr. Wiener establishes a very general theorem by means of Fourier integrals and deduces a great variety of Tauberian theorems in chapter III. Two important applications, treated in this chapter, are to the Prime Number theorem and the theorem on the 'mean-square' modulus of a function.

The last chapter is on generalised harmonic analysis and almost periodic functions. The latter subject has been treated at length in the work of Besicovitch published last year. Bohr's fundamental theorem that an almost periodic function can be represented by a generalised Fourier series is proved here by a comparatively simple method.

The work is an important and welcome addition to mathematical literature and we may express a hope that the author may find time to give us an exhaustive and systematic treatise on the subject in the near future.

N. M. S.

**Mass Spectra and Isotopes.** F. W. ASTON, Sc. D., F. I. C., F. R. S., Arnold and Co., 1933.

This volume deals with a subject which the author has made peculiarly his own. It incorporates the substance of lectures delivered at the University College of Wales, Aberystwyth, on the Aberystwyth Lecture Foundation during the Session 1931-1932. Part I is historical, Part II is mainly experimental and deals with the Production and Analysis of Mass-Spectra, Part III gives an account of each individual element relative to its isotopic constitution developing the new science of "nuclear" chemistry. The rapid progress in the artificial transmutation of elements is bound to render increasingly valuable this collection of data. Part IV is theoretical and discusses the implications of the results which have been obtained by the use of the mass-spectrograph.

It was in 1912 that the application of the method of positive ray analysis to neon indicated the existence of isotopy among the non-radioactive elements. With the completion of the mass-spectrograph in 1919 the non-homogeneity of neon was confirmed and a few weeks later the isotopic complexity of chlorine and mercury was demonstrated, and the whole number rule formulated. Progress since then has been continuous

until in 1932 the hydrogen isotope of mass 2 was discovered, and at present, out of all the elements known to exist in reasonable quantities, only eighteen remain without analysis. Of these eleven are rare earth elements.

The discovery of the heavy isotope of hydrogen is of particular interest. It has recently been found that heavy water from the heavier isotopes of hydrogen and oxygen can be concentrated by electrolysis, and in the *Journal of the American Chemical Society* for October, 1933, some of the properties of this water have been listed. Its density is over 1.1 and its viscosity some 40% greater than that of ordinary water. Heavy water appears to be toxic to fresh water organisms.

This fascinating book on a new and fundamental branch of Chemistry by one who is responsible for practically all the developments of the subject discussed is certain to become a classic. It is written in a clear and simple style and can be recommended alike to the student, the general chemist and the isotope specialist.

T. S. W.

*Introduction to Thermodynamics for Chemists.* D. JOHNSTON MARTIN, B. Sc., Ph. D., Arnold and Co., 1933.

This book is a complete introduction to modern thermodynamics for chemical students. Besides dealing with the fundamentals of the subject, it includes chapters on Lewis' "Activity" method of treatment of solutions on the modern theory of strong electrolytes, and on the Third Law of Thermodynamics. The treatment is up-to-date and references to the original literature are given. In some instances statements made in the literature have been accepted in an uncritical manner but a book covering so wide a field must naturally be more of a compilation rather than a critical monograph.

Thermodynamics is probably the most difficult subject a chemical student has to study; in no subject is he more dependent on the skill of his teacher in imparting accurate and fundamental knowledge. The student must always be clear as to the quantities under discussion, their signs, and the conditions under which the alterations in these quantities occur. The interests of the average physical chemist are not, however, in the more mathematical portions of his subject, with the result that too often, the subject is badly taught due to vagueness on the part of the teacher as to what he is really teaching. In desperation the student crams for his examination and disgorges lumps of mentally undigested matter on the examiner in answer to book-work questions leaving

numerical examples and the development of book-work severely along. Once the examination is passed, thermodynamics is forgotten.

This book, therefore, will be useful to the teacher rather than the student. For the beginner its utility could be improved by the introduction of general questions and numerical examples at the end of each chapter, and by the provision of a table of symbols at the beginning. It would be of advantage also if some of the industrial applications of Thermodynamics had been considered.

T. S. W.

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Publications of the Bureau of Economic and Social Research, Sun-Yatsen University, Canton, China.

*Review of the Academy of Philosophy and Religion*, Poona, India.

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# Journal OF THE University of Bombay

[ BIOLOGICAL SCIENCES, INCLUDING MEDICINE ]

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VOL II

MARCH 1934

PART V

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## THE BIONOMICS, MORPHOLOGY, AND METAMORPHOSIS OF MELIPONA IRRIDIPENNIS

By

C J GEORGE, M.A., Ph.D, D.LC

*Professor of Biology, Wilson College, Bombay*

### *Observations on a hive.*

In February 1924, I happened to find a hive of *Melipona irridipennis* in a crevice on the wall of my house at Coimbatore. As no account of this bee was available from India, I proposed to make a study of it. As long as the hive was situated inside the wall, observation was impossible, and so I very much desired to have the bees transferred to a better situation. As they build irregular combs, transferring them to an ordinary hive was out of the question. It occurred to me to try whether the bees would take to a vessel of 12" diameter if it was fixed to the wall in such a way as to bring the entrance of the hive inside the vessel. An earthen vessel was fixed on the wall and a small hole about  $\frac{1}{4}$ " in diameter was made on the lower side of the vessel to serve as an entrance.

The bees were a little alarmed at this sudden alteration of the surroundings, but in the course of two or three days they made themselves quite familiar with the additional space and were making use of the new entrance. But it took about eight weeks for them to be convinced of the reliability the new hive offered to them. By cutting off a piece 3" x 3" from the earthen vessel on one side and replacing it with black paper pasted on the outside, a crude but very useful doorway for making observations was made. An electric torch light



had to be used for illuminating the hive, though it caused a certain amount of disturbance among the inhabitants.

The first step in the conversion of the vessel into a hive was the construction of a tubular entrance with the sticky material made of wax and earth known as "cerumen." This was accomplished by the third day. Three or four workers were invariably posted at this entrance as sentries. Nothing more was done till the next April. During the course of my usual examinations one day I noticed that a certain amount of wax was fixed up in the small crevices left between the pot and the wall. This work was done with such speed that during the course of three days the bees had begun to build the foundation of pollen combs. During the course of the succeeding week about two dozen pollen cells were constructed, a good number of which were also filled. Obviously the favourable Summer season had much to do with this enormous output of work. The next step was the construction of honey cells which were erected on the roof, separate from the pollen cells. The appearance of the honey cells was so deceptive, as not to attract my attention until their number grew up to about half a dozen. Soon after, the foundation of the brood cells was also made out in the right half of the vessel. In the course of a few days a huge cluster of beautiful cells was constructed and in some of them eggs were laid. I could not observe the queen at work as she would disappear from the surface of the brood cells as soon as I would open the hive. By the end of April a well established colony was inhabiting the new hive. New pollen, brood and honey cells were added one after another and the first set of workers hatched out by the last week of May. New individuals were added to the colony every day and by July the colony was enormously strong and the whole hive was filled up with brood, honey and pollen cells. Every time the paper door was closed after an inspection the workers glued it with wax.

Towards the close of July the monsoon broke and it took an enormous toll of the colony. As the number of workers was reduced the food supply was not replenished at the same rate it was used up. After some time therefore there was a lull in the production of new brood cells. But mention should be made of the few workers hatching out every day. Amongst the existing brood cells of that time, there were a few larger than the ordinary ones and one of them was particularly large.

On the 17th of August, one of these big cells opened and the others followed the next day. It was not possible to recognize the newly hatched individuals from the larger cells amongst the large number of workers. On the 21st, while examining a few bees lying dead on the floor, I found to my surprise that there were two drones

amongst them. Probably the workers had killed and thrown out the newly hatched drones from the larger cells. The largest cell of the lot was possibly a queen cell and the queen was also presumably killed. By the second week of September, as the monsoon stopped, a revival of activities began and the breeding went on as vigorously as ever. The honey and the pollen stores which were almost used up during the bad season were soon replenished. But occasional spells of rain seriously hampered the continued progress of work in the colony.

Then came the Winter months, December, January and February. Though Winter is not severe at Coimbatore, there was a slowing down of the activities of the bees. The glorious Summer of 1925, with its beautiful blossoms everywhere, followed. The little artisans made the best use of the season and one could hear so well the hum of the hive. A long stream of workers was going in to unload their burden of pollen and honey. On the 28th of June I removed the the vessel from the wall and, without disturbing the brood cells, cut out the honey combs, leaving only a few. These combs yielded about four ounces of honey, a quantity double that of an ordinary hive from inside a decayed tree or a wall. The young workers greedily made a feast of the honey spilled while removing the combs. The wax of the combs was restored to the hive and the vessel was fixed in its original place. The hive was not disturbed for a week, and when I opened it next, I found that everything was in order. The honey which was left in the hive was either used up or devoured by the workers. The wax that was returned to the hive was converted into thin sheets and spread inside the hive.

On August 18th 1926, I removed the whole hive as I was leaving Coimbatore and, on examination, found that the crevice inside the wall was still retained as part of the hive with brood, pollen and honey cells. Though almost two months had elapsed since my removal of the honey combs, not a single honey cell was constructed in place of those removed, but among the pollen combs were found twelve honey cells. There was only one queen, which was hiding among the brood cells inside the crevice on the wall and there was a drone, only a few hours old. It is concluded from the above observations on the hive that the honey season is from March to June and that this season is also the season for prolific breeding. This further supports my observations in South and Western India on *Apis indica* that Summer is the only honey season. Supplies of honey from the hills also lead to the same conclusion.

#### *External morphology of the adult.*

See the Fauna of British India, Hymenoptera Vol. I., p. 563, for a detailed account of specific characters. The following features of external morphology may however be of interest,

The worker is a small dark creature of 3-4mm. in length. The queen is similar to the worker in its morphology but larger in size and paler in colour. The drone is but slightly larger than the worker and so is difficult to be distinguished from the latter. He differs from the queen and the worker in having twelve segments to the flagellum of the antenna, while the latter have only eleven.

The head is round, the antenna is typically Hymenopteran with a scape and flagellum. The flagellum is provided with numerous sub-circular or oval pits with hairs which are regarded as sensory in function. The maxillae and the labium are folded on themselves, the former at the junction of the cardo and the stipes, and the latter at the base of the ligula. The folded organ fits into a groove on the ventral side of the head when at rest. The folding of the maxillae and the labium afford full free play to the mandibles which lie above. The maxillae bear rudimentary 2 jointed palps. The lacina are placed in close approximation to the basal portion of the stipes which is a well developed structure. The labial palpi are five jointed. (Vide Fig. VI).

The hind tibia is enlarged to function as the corbicula or pollen basket. The usual two kinds of hairs, simple and branched, occur all over the body. The branched ones are of use in collecting pollen. The hind wings interlock with the fore wings by means of five hamuli. (Vide Figs. II & III).

A functional sting is absent, but the parts are present in vestiges, as shown by von Jhering, and they are more pronounced in the queen than in the worker. The 7th abdominal segment is the last visible one and all the segments behind it are telescoped into it. The 7th sternum is bifid posteriorly and if it is turned over, the concealed segments are revealed. On either side a pair of characteristic plates bearing spiracles is seen inside the 7th segment. These plates have been shown in the honey bee to be part of the 8th tergum by Zander. Mesially there is a pair of plates which corresponds to the "oblong plates" of the honey bee bearing distinct palps. On the inner faces of these are present elongated structures representing the sheath of the honey bee sting or the inner ovipositor lobes of other insects. The anterior ovipositor lobes or the lancets of the honey bee sting, are also present as vestigial structures. (Vide Fig. VIII).

In the male the 9th segment bears a median aedeagus on either side of which is a well chitimized paramere. The gonocoxite is present and shows a basal cardo and a distal stipes regions. *Melipona* differs from *Apis* in the fact that parameres are absent in the latter. (Vide Fig. VII).

*Life-history and bionomics.*

Swarms are given off from the older hives usually in August or September in Coimbatore. This corresponds to what is obtainable in *Apis indica*. In other parts of India this may depend on the incidence of the monsoon. I have never noticed a new colony settling down, but I happened to observe one soon after it had occupied a small crevice in a wall. There were about a hundred workers, which were coming out and depositing small pieces of mortar at some short distance from the hive.

The brood combs are constructed on pegs of wax fixed to the wall, and by the addition of new pegs and new cells an elaborate maze of brood combs is established. (Vide Fig. I). The wax is of a dark brown colour and very soft to the touch. A brood cell is roughly  $3\frac{1}{2} \times 2$  mm. Each cell is half filled with a mixture of honey and pollen, and when a thin film is formed on the surface of this viscid mass, an egg is laid in a perpendicular position and the cell is closed. The egg and the larva do not sink in the liquid and thus keep in touch with the air enclosed in the cell. (Vide Fig. IV). The egg is about 1 mm in length and  $\frac{1}{2}$  mm across. It takes four or five days to hatch out. The newly hatched larva is 2 mm. long and is a delicate, almost transparent, creature. The full grown larva is 5 mm. long and is rather stout in appearance. The feeding larva is transparent yellowish brown in colour due to the food in the alimentary canal, while the pupating larva and the pupa are opaque white in colour. Before pupation it spins a white cocoon and the adult emerges by piercing this cocoon, which by that time has adhered to the waxy cell. It takes three to three and a half weeks from the egg to the adult stage. The brood cells show slight variation in size and the newly hatched workers also exhibit a corresponding variation in size. The queen cell is the largest and is therefore easily recognized. The drone cell is slightly larger than that of the worker and is difficult to distinguish from the larger worker cells. In a hive apparently at a time never more than two queen cells are constructed, but there may be as many as ten drone cells.

The pollen and honey cells measure about 7 or 8 mm. in length and  $3\frac{1}{2}$  to 4 mm. in thickness. They are constructed in rows fixed to the wall without any intervening pegs. (Vide Fig. I). The pollen store varies from light bright yellow to dark brown in colour, the bees chiefly visiting plants with abundance of pollen, such as the Graminaeae. The honey is of pale yellow colour but a tinge of pollen gives it a beautiful red colour and it is almost impossible to collect this honey without some admixture of pollen, as honey and pollen cells are constructed together. The honey has a sweet slightly sour taste. These

bees are exceedingly tame and freely enter the flower shops. They also visit the sweetmeat shops to collect the sugary juice present in some kind of sweetmeats.

The entrance to the hive is a narrow circular hole, the wall of which is made of "cerumen" which projects about half an inch to the outside. (Vide Fig 1). A few workers guard the entrance, their number varying according to the circumference of the entrance. The tubular entrance does not directly lead to the hive, but terminates in a round cavity from which there are two inlets, one to the broad combs and the other to the honey and pollen combs. This round about entry to the hive may serve two purposes, the prevention of direct light which these insects abhor always and the sudden invasion by any enemy. There is a network of paths under the brood cells to facilitate easy access to any part within the hive. This is very necessary as the brood cells from which adults have emerged are destroyed at once and new ones constructed. Very soft wax is used for making the cells but harder wax is used to close any crevice or to strengthen any weak spot in the hive. Any wax found outside is assiduously collected and deposited in some part of the hive, without it ever interfering in the normal working of the hive.

I have not observed any parasites or predators of these bees, but a species of *Megachile* sometimes visits the hive and snatches off some wax from the entrance.

#### *The larval anatomy.*

The mature larva is rather stout and lies bent on itself in the cell. The external cuticle is very thin. The narrow head segment is followed by 13 segments.

*The central nervous system.*—The central nervous system consists of supra-oesophageal ganglia or brain, situated in the posterior region of the head, and a double ventral nerve cord of 11 distinct ganglia situated in the first eleven segments of the body. The last two segments have no ganglia but are innervated by nerves from the eleventh. In section a ganglion exhibits an internal medullary region and an external region of ganglion cells and the whole is covered by a thin enveloping membrane. (Vide Fig. IX).

*The digestive system.*—The buccal cavity opens into a short pharynx which is connected to the midgut by a narrow oesophagus. The hindgut lies bent on itself below the midgut, its anterior end being in contact with the posterior end of the midgut. There are four thick malpighian tubules which take their origin from the hindgut at its junction with the midgut.

*The silk glands.*—There is a pair of silk glands situated ventral to and on either side of the alimentary canal, extending posteriorly to

the 8th abdominal segment. The two glands unite in the region of the suboesophageal ganglia and passing below these open on the lower lip. The duct of the glands opens between two dorso-ventrally flattened spiny processes which appear like a pair of forceps in longitudinal sections. The gland shows a layer of large epithelial cells and a central canal running through the whole length. (Vide Fig. IX).

*The respiratory system.*—There are ten pairs of spiracles, two thoracic on the meso- and meta-thorax, and eight abdominal on the first eight abdominal segments. The spiracular opening leads to an atrium which narrows at its proximal end and opens into a short trachea. The short trachea takes a ventral transverse course and opens into a longitudinal main trunk. The two main trunks are connected anteriorly and posteriorly by transverse trunks. At the junction of the spiracular tracheal branch and the main trunk, smaller tracheal branches are given off.

*The vascular system.*—The hemocoel is mostly occupied by the fat body. The fat body consists of round or hexagonal cells very closely packed together. Each cell has a central nucleus and a clear cytoplasm showing a number of vacuoles. Imbedded in the fat body are a few oenocytes which in sections appear in all sorts of shapes varying from triangular to circular.

*The gonads.*—Lying dorsally in the worker is a pair of ovaries in the 5th abdominal segment. Anteriorly the enveloping layer of the ovaries is continued as a narrow strand which extends upto the 4th abdominal segment. The male gonads have not been studied.

#### *Metamorphosis.*

1. *The imaginal buds.*—In the mature larva there are in the head imaginal buds representing the antennæ, compound eyes, mandibles, maxillæ and labium. In the thorax there are three pairs representing the legs, and two pairs foreshadowing the wings. There are also thickenings of the hypodermis in segments 8 and 9 representing the gonapophyses in the worker larva. The hypodermis of segment 7 also shows a slight thickening on the ventral side. (Vide Fig. IX)

2. *The nervous system.*—It has already been stated that in the mature larva there are 11 ganglia on the ventral nerve cord, 3 in the thoracic and 8 in the first eight abdominal segments. According to Nelson there are 11 ganglia in the abdomen in the embryo of the honey bee in the early stages and in the later stages the 9th, 10th and 11th unite and come to lie in the 9th abdominal segment. During the early larval life the terminal ganglion unites with the preceding one and lies in segment 8. Thus the larval nervous system is derived. The number of ganglia in the mature *Melipona* larva agrees with that

of the honey bee and presumably therefore the last ganglion in the 8th abdominal segment is a compound one representing segments 8, 9, 10, and 11. During the early stages of metamorphosis, which is soon after defaecation, the 1st abdominal ganglion moves forward and fuses with the metathoracic one. During a later stage when the limbs and the mouth parts are about to unfold from the imaginal buds, the 2nd abdominal ganglion is seen about to fuse with the one in front. At this stage the penultimate abdominal ganglion, the 7th, fuses with the preceding one and comes to lie in segment 6. During the pupal stage, the compound ganglion of the metathorax and the mesothoracic ganglion fuse together. Thus in the adult there are 2 thoracic and 5 abdominal ganglia. The fusion of the ganglia takes place by the gradual absorption of the intervening cord. The 1st thoracic ganglion is situated in the prothorax and innervates that segment. The 2nd thoracic ganglion is situated between the meso- and meta-thorax and innervates these two segments, and also the 1st and 2nd abdominal segments. The first free abdominal ganglion (i.e. the true 3rd) though situated in the 2nd abdominal segment, properly belongs to the 3rd abdominal segment and therefore innervates that segment. The 2nd and 3rd abdominal ganglia situated in abdominal segments 3 and 4 respectively innervate segments 4 and 5. The 4th abdominal ganglion is formed of the true 6th and 7th and is situated in segment 6 and innervates segment 6 and 7. The last ganglion is situated in segment 7 and innervates segments 8, 9 and 10. Snodgrass in the "Anatomy and Physiology of the Honey Bee" states on p. 293 that in the adult honey bee the penultimate ganglion is formed by the fusion of the true 6th and 7th ganglia. This is true of *Melipona* as well as *Apis indica*. But he fails to reconcile the adult anatomy with the changes taking place during metamorphosis. According to him (vide p. 273) the penultimate ganglion of the adult bee lies in the 6th segment of the abdomen and innervates that segment. Specimens of *Apis dorsata* and *indica* were dissected to see if the above statement was correct. It was found that the 6th abdominal ganglion gave rise to two pairs of nerves, as might be expected from its composite nature, of which one pair innervated the 6th segment and the posterior pair the 7th segment. (vide Figs IX and X). Snodgrass' description on p. 273 is therefore obviously incorrect. His figure however is correct.

3 *The digestive system.*—At the beginning of pupation the posterior region of the midgut, where it is pressed against the hindgut, breaks down and the faecal matter stored up in the midgut is passed to the outside. The malpighian tubules which in the larva do not possess any opening at all, also come to open and empty their contents into the gut. As a natural consequence the gut and the malpighian

tubules shrink. Histolysis of the epithelium of the gut soon follows and this results in its eventual absorption. A layer of new epithelium, which was already growing around the old one, takes its place. The fore- and hind-guts also undergo the same process of degeneration and regeneration. The foregut soon after widens out and its epithelium becomes developed into a layer of deep columnar cells. Where the foregut meets the midgut the former enlarges into a structure which gradually develops into the so-called "honey stomach". The malpighian tubules of the larva degenerate and disappear entirely. With the degeneration of the larval tubules, imaginal tubules are budded off from the regeneration area of the hindgut. The hindgut which was a bent tube lying beneath the midgut in the larva, becomes a straight tube during the early stages of metamorphosis. The anus which was situated at the posterior extremity of the long axis of the body in the larva, has now come to lie on the ventral side. During the late pupal life the hindgut widens out at its posterior region and this ultimately develops the rectum with its elaborate system of glands.

4. *The silk glands*—The silk glands undergo complete histolysis and disappear entirely.

5. *The fat body*—The larval fat body cells show a central nucleus and a vacuolated cytoplasm when stained with Mallory's Triple Stain. But the fat body of the pupating larva when stained with the same stain shows a number of globular bodies in the cytoplasm, some stained red, some reddish blue and others light blue. These bodies according to Berlese and others, are albuminoids occurring in different stages of elaboration. The fat body cells soon lose their cell membrane and these globules are thrown out into the blood. Sections of pupæ show that most of the fat has been used up during metamorphosis, there being only a few cells and globular bodies left floating in the blood. The oenocytes embedded in the fat body are liberated when the latter breaks up. They assume more or less a globular form and eventually seem to undergo degeneration. There is considerable difference of opinion regarding the fate of the larval oenocytes. According to Koschevnikov (1900) and Weisenberg (1907) the imaginal oenocytes arise from the hypodermis during the pupal stage, most of the larval ones degenerating entirely. Perez (1903) however states that Koschevnikov's observation is erroneous. In *Melipona* a large number of small oenocytes are seen near the hypodermis during the early pupal stage, and these differ considerably in size and staining qualities from the larval oenocytes. There is every reason to suppose that these are the newly formed cells which persist in the adult as imaginal oenocytes. Thus my observations support those of Koschevnikov.

Mention should be made of another set of cells which make their



appearance during the pupal stage. They are completely absent in the larva and they make their appearance during the prepupal period, and are limited to the abdominal region. These modified fat cells are characterized by their large size, being visible to the naked eye as dark bodies amidst the fat body in the pupating larva. There is a central nucleus with a granular cytoplasm and a thick cell membrane. The cytoplasm does not absorb any stain.

Many workers seem to have noted these cells but apparently have regarded them as oenocytes. Karawaiew (1898) describes in *Lasius* a set of large phagocytes and his description of these cells fits in very well with the cells described above. I have not been able to observe any phagocytic tendency in these cells which I have described. They show certain inclusions in the cytoplasm which appear to be excretory products. In the adult they become crowded to the posterior region of the abdomen and finally seem to disintegrate. Their cytoplasm shows also a general resemblance to that of nephrocytes, and I have therefore preferred to call them pronephrocytes. (Vide Fig. IX).

6 *The female efferent genital system*—It has been said above that the oviducts terminate on the ventral side of the 7th abdominal segment in the larva. During the early stages of metamorphosis three ventral hypodermal thickenings which ultimately result in three invaginations develop. The first of these is from the anterior region of segment 8, and is the vaginal invagination. Such an invagination has been noted by Nel in *Locustana* in the same situation. Morphologically therefore it is homologous to the invagination in Orthoptera and Homoptera. This invagination as it grows forward becomes dorso-ventrally flattened anteriorly. Later on its dorsal and ventral walls meet and fuse along the median line at the anterior half. This results in the formation of two ducts at that region. These two ducts meet the oviducts of their respective sides and during the later pupal stage fuse with them. Thus the female efferent system is established.

Meanwhile the second and third invaginations also elongate, the latter showing more pronounced growth than the former. The former takes its origin from the median ventral side of the 8th segment behind the rudiments of the anterior ovipositor lobes. At its posterior extremity it opens into a groove which later on extends anteriorly and posteriorly till it meets the other two invaginations. The second invagination is that of the spermatheca. As pupation proceeds the hypodermis intervening between the first and second invaginations shrink in such a way as to approximate the two invaginations. At the same time the ventral wall of the vaginal lip grows posteriorly thereby shifting the vaginal opening backwards. As a result of these changes the spermathecal invagination not only becomes confluent with the vagina

but comes to lie on the dorsal side of the vagina. This is the condition in which it is found in the adult.

The third invagination takes its origin between the rudiments of the ovipositor lobes and elongates anteriorly until it occupies an oblique position in the body cavity. A short distance from its opening it widens out into a sac, though at the anteriormost region the lumen is narrow. This is the rudiment of the acid gland. The wider region develops into the reservoir of the gland. (Vide Fig XI). In the worker the efferent system occurs in a less developed condition than in the queen.

Snodgrass figures and describes the vagina as opening at the anterior region of the 8th segment and anterior to the anterior ovipositor lobes in the pupa. Seurat also places the vaginal opening at the anterior region of the 8th segment. Tiegs places it further back between the first and second pair of appendages, *i. e.*, between segments 8 and 9. In the adult Hymenoptera the vagina opens in the situation described by Tiegs. The above described mode of formation of the oviduct and the consequent shifting of the vaginal opening to the 8th segment recalls the process which I have described in the case of Homoptera in an earlier paper (Q J M S, 1929). In Homoptera the original vaginal opening which is behind the 7th corresponds to the vaginal opening during the early pupal stage in *Melipona*. But none of these workers has studied the development of the common oviduct in detail and thus they failed to notice the shifting or carrying back the female opening behind the 8th. The spermatheca is regarded by these workers as an outgrowth of the vaginal invagination, in *Melipona* it is a distinct invagination in itself and opens independently of the vagina as noted by Zander in *Apis*, though subsequently it becomes fused with the vagina. The development of the spermatheca is exactly on the same lines as in Diptera, noted by Christophers and Baraoud, and in Orthoptera, noted by Nel.

One significant fact is that the sting glands are present though the sting itself is vestigial and non-functional. This compels us to assume that these glands are functionally female accessory glands. In Apidae the secretion from these glands containing formic acid prevents putrefaction and growth of moulds in honey and pollen store. Possibly similar use is found for them in *Melipona*. The ovipositor lobes are not properly developed occurring only as rudimentary structures. Tiegs regarded the genitalia of *Nansonia* female as having developed out of segments 8, 9, and 10, and states in that connection that such a development is in accordance with what Dewitz found in Locustidae. Obviously Tiegs has misinterpreted Dewitz who stated that the inner ovipositor lobes appear as processes from lateral lobes of the 9th segment,

### Summary and conclusions.

1. A general account of the life history and habits of *Melipona irridipennis* is given. It has been observed contrary to the general conception that hot months from March to July form the period of great activity as was noted in the case of *Apis indica* and *dorsata* in another connection.

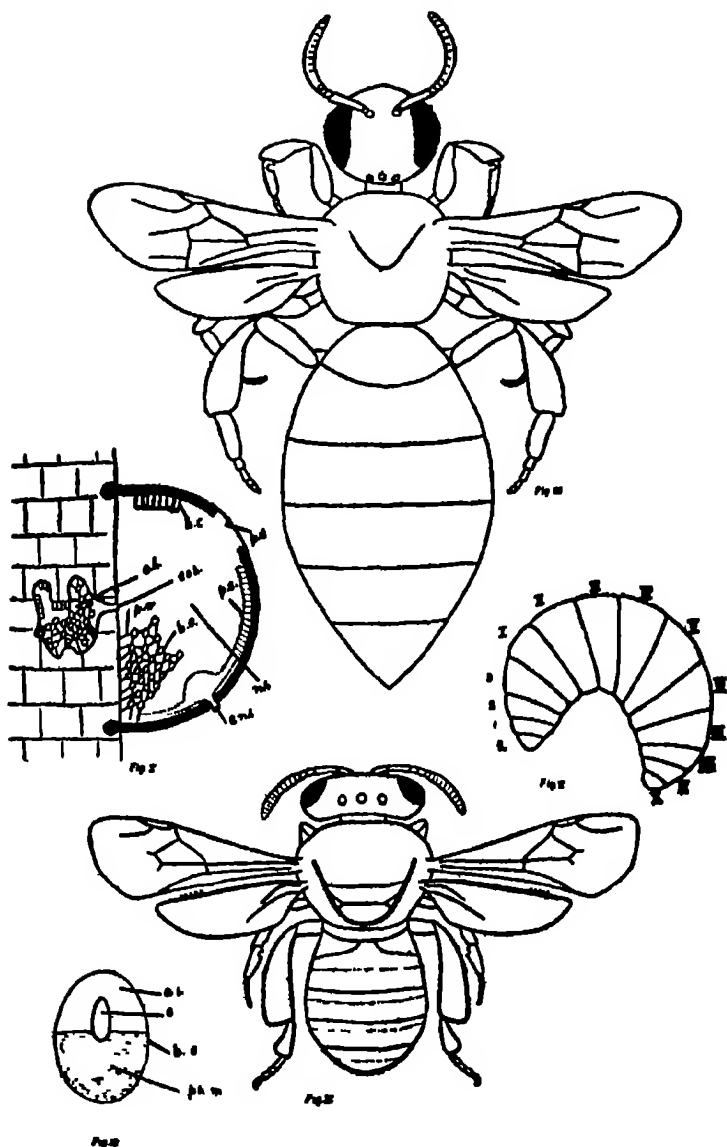
2. The general morphology of the worker is given. Larval anatomy and metamorphosis has also been worked out. Special features are (a) A few fat cells become modified as excretory cells during metamorphosis (pronephrocytes), (b) The adult oenocytes are formed from the hypodermis of the pupa, (c) The larval nerve cord with three ganglia in the thorax and eight in the abdomen becomes modified into a cord with two ganglia in the thorax and five in the abdomen when the adult condition is reached. The composite nature of the penultimate abdominal ganglion is established on anatomical and developmental grounds, (d) The formation of the female efferent system has also been studied, and it has been found that it takes place on the same lines as in Homoptera (George, and Metcalfe), and Orthoptera (Nel). The accessory glands (the poison glands) are present though the sting has become non-functional. It has been inferred therefrom that these glands are ancient structures of physiological importance in connection with the reproductive habits of the animal and their function as poison glands is a secondary modification. Such glands arising from the 9th abdominal segment are present in Homoptera and Orthoptera, etc.

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## EXPLANATION OF DRAWINGS.

- Fig. I. A diagrammatic section of the hive of *Melipona irridipennis* kept under observation  
 Fig. II. The worker of *Melipona irridipennis*  
 Fig. III. The queen do.  
 Fig. IV. Egg in situ in a cell do.  
 Fig. V. The larva do.



Fig. X. The nervous system of the adult, *Melipona irridipennis*.  
(semi-diagrammatic)

Fig. XI A vertical longitudinal section of the hind region of the  
abdomen of a pre-pupa, do.

### LETTERINGS.

1. 2. 3.	Thoracic segments.	l p	Labial palp
I to X.	Abdominal seg- ments	m	Mouth.
a.	Anus.	m d	Mandible
abd g. 1st-5th	1st to 5th Abdo- minal ganglia.	m.g	Mid gut
aed.	Aedeagus.	m l.	Malpighian tubules of the larva.
a.g	Acid gland	mx.	Maxilla.
a.n	Antennary nerve.	mx p.	Maxillary palp
a.o.l.	Anterior oviposi- tor lobe.	n.h.	New hive
a.s.	Air space in the cell	o.d.	Oviduct
b	Brain	o.h	Original hive on the wall.
b.c.	Brood cell	oe.l.	Oenocytes of the larva.
c.	Gono-coxite of the male.	o.s.l.	Opening of the silk gland.
e	Egg.	p c.	Pollen cells.
e.n.h	Entrance to the new hive.	p d	Paper door.
e.o.h.	Entrance to the old hive.	p h m	Pollen honey mixture
f	Fat body	p v.	Pegs of wax to which brood cells are attach- ed.
h	Head	s.g.	Sub oesophageal gang- lion.
h c.	Honey cells.	s.gl.	Silk gland.
h.l.	Hind intestine	spi.	Spiracle.
l.o.l.	Inner ovipositor lobes.	sp.	Spermatheca.
l.	Ligula.	th.g 1st	1st thoracic ganglion.
l.o.l.	Lateral oviposi- tor lobes.	th.g.2nd.	2nd thoracic ganglion.
		v.	Vaginal invagination.
		v.n.	Ventral nerve cord.

# DEVELOPMENT OF THE TROUT SCALE

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(With 4 plates)

## Introduction.

The following paper contains an account of an investigation on the development of the Teleostean scale, chiefly that of the Trout, *Salmo fario* and *Salmo irrideus*. The Teleostean scale has been studied by a large number of investigators, [Leydig (1851), Baudelot (1873), Hofer (1889), Klaatsch (1890), Ussow (1897), Tims (1902), and more recently by Hase (1912), and by Paget (1920)].

Klaatsch's (1890) account of the development of the Teleostean scale, although supplemented by the work of others, has remained the standard authority. In the interpretation of the several details there is, however, an entire lack of agreement. The accounts of different investigators vary to an extraordinary extent in the matter of detail, this is largely due to technical methods of investigation, e g., the scale being an extremely hard structure there is great difficulty in cutting it into thin sections.

The literature on the subject has been reviewed very thoroughly by Stuart (1904) and Paget (1920). The latter author in his review presents points from the work of other investigators where lack of agreement exists; I shall go into these details later, and, while discussing the more important points, shall refer to the work of the several authors.

For the suggestion of this problem and for much valuable advice I am greatly indebted to Mr. J. Gray

## Methods

### (a) General fixing and staining methods.

The material was fixed in at least four fixing reagents, viz. Bles' fluid, corrosive sublimate, Fleming without acetic, and Boun's fluid. I found Bles' fixative very satisfactory, giving good fixations.

Great difficulty was experienced before satisfactory preparations were secured, it is by no means easy to obtain preparations in which the cell-boundaries and cell-layers are sharply differentiated. Several stains were employed to bring into evidence the intercellular network,



and were abandoned as unsatisfactory, for the scale-layers proved unusually difficult objects for cytological study.

Of the methods employed, the silver impregnation gave the best results, the only difficulty being that the nuclei in such preparations did not take up the stain, the cell-boundaries are, however, shown with special distinctness, which made it possible to distinguish between the different cell-layers

(b) Special method

The scales to be impregnated must be fresh, that is, such as have not been treated with any reagent. It is only fresh scales which will impregnate.

The fresh scales are first washed in distilled water containing a trace of sodium sulphate (0.75%) for 2 or 3 minutes. They are then transferred to silver nitrate 0.2% solution for 5 minutes, after this they are again washed in distilled water. After this washing they are developed in any clean developer, (e.g., Amidol 0.2% in 2% sodium sulphate diluted with water 5 or 6 times, from 2 to 3 minutes).

After a final washing in distilled water, the scales are mounted in glycerine.

*Material.*

The numerous specimens of Trout used during the course of the investigation were obtained entirely from Nailsworth in Gloucestershire. These were sent alive to Cambridge.

*Description of Scale Development*

(a) Early appearance.

The first stages of scale development take place in fish larvae of about 3 cms. in length and when the fish is about 75 days old. The trout material obtained from Nailsworth proved remarkable in that the fish, growing under practically identical conditions in tanks, showed great variation in size. It was found that some fish grew much more rapidly than others and fish of the same age varied markedly in size. The first scales to appear were those of the lateral line. Certain relatively large fish occasionally showed no trace of scales. Such individuals were, however, extremely rare. Attention has been very often drawn to the close relationship between the scales and the age of the fish, the study of the scale development in the trout shows that the scales do not appear uniformly over the whole body, and the scales from different regions show variation in the number and even width of annuli. It may be mentioned that, in the early stages, in between the fully developed scales, one also comes across smaller scales with fewer lines of growth. These small scales are mentioned by Klaatsch. This irregularity is very marked in some of the fish, but as growth proceeds one rarely meets with it.

The first indications of the formation of the scale are seen in the outer part of the dermis, in which appear a series of cell aggregations; an early sign of development is the frequency of mitotic and amitotic figures in the region below the basement membrane of the epidermis. This continued activity results in the production of hillocks as seen in Fig 1. In transverse sections, several layers of cells are seen at this stage. The cells in a cluster have large nuclei and each has a deeply stainable protoplasmic body. Each of these clusters extend laterally and represent flattened papillae. At this stage the dermis differentiates into two layers, an outer spongy and an inner fibrous layer, these two regions merge into each other, there being no distinct boundaries.

The first indication of the appearance of the scale itself is a thin sheet of a highly refractive substance, the scale at this stage is symmetrically enveloped by the dermal cells which on their outer side appear several layers deep (Fig. 8). These cells, to which Klaatsch has given the name of "*scleroblasts*", separate the scale completely from the epidermis, which never takes any part in the development of the scale, very often the scale lies in the epidermal region of the body, this occurs as a result of oblique cutting of sections. While the above changes are taking place, Hofer (1889) and Hase (1907) believe that the basal epidermal cells undergo a remarkable alteration. According to these authors, in the trout the basal layer of the epidermal cells, which lie immediately over the developing scale, become modified to form an enamel membrane, though the structure never becomes functional. Later they reassume their original form, losing this special character. Hofer attaches to this fact considerable phylogenetic interest because in the development of the Ganoids and the Placoids the larger portion of the spine is epidermal. In the Teleostean scale, the scale takes its origin in the dermis, and throughout life remains a dermal structure. Hofer and Hase see in this fact an indication of ancestral condition, According to Paget the epidermal cells lying immediately over the young scale become cylindrical although the change is not universal. I have gone through all the preparations with special attention to this point, but in no way have I been able to find structures corresponding to those described by Hofer and Hase. In the course of very early development, the epidermal cells appear to be slightly more cylindrical in form. I have not noted a similar change in the course of formation of the scale. As for the enamel organ itself, it occurs in advanced stages, so that the very early assumption of cylindrical appearance seems to me to be against its morphological significance. If it does occur in the later stages, it may be a transient phase or perhaps indicate a phenomenon that occurs very rarely, and it would be best to regard as artefacts such changes in structure which occur so rarely.

In both *S. fario* and *S. irrideus* there is present below the basal epidermal layer the basement membrane, which in *S. irrideus* is strongly developed and well marked (Fig. 2). The basement membrane appears to be double in nature, this appearance is due to the existence of a definite membrane and the presence of fine ectoplasmic layers of the basal epidermal cells, which, when continuous, present the form of a second membrane.

(c) *Cell layers, their arrangement and behaviour.*

In thin sections of Trout embryos at this stage, the layer of cells on the dorsal surface is seen to be several cells deep, as growth proceeds, the depth of the cells is reduced and one always meets with two distinct layers on both the surfaces (Figs. 5, 7, 9) the scale makes its appearance in between these four layers. The cells in these layers in the act of secretion undergo certain definite changes whether the secreting cells are from the dorsal or from the ventral surface, the behaviour and modifications undergone are essentially similar in both cases. My preparations indicate that the cells and their nuclei grow considerably and become transparent. The nuclei of the dorsally placed cells become very much flattened and change gradually from a circular to a broadly conical form, the karyosomes break up into irregular fragments giving a granular appearance to the nuclear contents very different from the first. During this activity the cells with their nuclei remain attached to the scales between the concentric striations. (Fig. 14.) The fusion is so intimate that in sections the presence of cell walls associated with the nuclei may be demonstrated with very great difficulty.

The nuclei in the dorsal scleroblasts when they are properly fixed with Fleming without acetic and stained with Iron haematoxylin show at certain stages whitish areas which are small in the beginning, but later become confluent to form one large area (Fig. 7). In the ventral scleroblasts similar very minute areas appear in the nuclei and seem to be of the nature of secretions which build up the substance of the scale.

Another interesting feature of the dorsal scleroblasts, which seems not to have been recognised, is that these cells are remarkable in being very passive. There are no signs at any stage of excessive cell multiplication taking place on the margins or on the surface of the scale. At the edge of the scale the upper and lower layers merge so intimately that no distinction can be drawn between them (Fig. 6). There is no sign of excessive cell multiplication on the dorsal surface, whereas on the ventral surface the same phenomenon is actively displayed, one meets with cells and their nuclei in various stages of development. It may be therefore that the cells are in process of migration

from the ventral surface, from which the dorsal scleroblasts receive fresh reinforcements; the new elements at the margin continue to become associated with the upper scleroblasts.

There is considerable divergence of opinion regarding the polygonal layer (of Klaatsch) of the scale.

Klaatsch records this layer as occurring on the dorsal surface "The superficial scleroblastic layer offers a very characteristic picture. Its polygonal-shaped elements simulate a flat epithelium. Between the protoplasmic bodies, which stain intensely in carmine stains (also in haematoxylin), there exists a network of a substance which does not tinge. This latter calls to mind a system of intercellular spaces." The histology of this cell layer was first studied by Klaatsch and the results of his investigations are contained in the following statements "It attains a longish form and the nucleus reaches a more peripheral situation in the cell. By this means the nuclei of adjacent cells frequently approach one another, a nucleus-containing part from a nucleus-free section. In the latter, the following occurs with great regularity. At one spot the protoplasm loses its staining capacity, while this part retreats further and further towards the circumference, there arises a bright, almost circular spot (of about 6" in diameter) which in form and size simulates a nucleus. Its interior shows no structure. While it stretches further and further towards the pole of the cell directed towards the nucleus, it eventually unites with the bright parts between the cells. The bright streaks between the cells owe their origin, just like the bright spots which I have described above, to a substance which has become differentiated from the remaining protoplasm." (Fig. 4.)

My interpretation regarding the nature and origin of the 'white spots' differs from that of Klaatsch, the origin of the white spots and his explanation of the elongation of the cells are not clear to me. It is evident in my preparations that the spot arises from within the nucleus (Fig. 4). The material from which it is derived is densely massed to one side of the nucleus, this loses its connection with the nuclear membrane, and moves away from it towards the centre of the cell. In its early stages the colourless mass simulates a nucleus, but later becomes diffuse and some of it no doubt unites with the intercellular substance, gradations between the early stages and the last stages are met with. It seems to me that the white spots certainly stand in genetic relation to the nucleus. In early, as well as late development, the nucleus is very closely surrounded by a whitish ring, this ring I think is a substance which is differentiated in the nucleus; it penetrates osmotically the nuclear membrane and becomes deposited round it in the form of a ring, giving to the nucleus the appearance of lying

in a large vacuole. This substance I consider as a secretion which accumulates round the nucleus and is finally eliminated in bulk.

If this derivation of the spots from the nucleus itself is not correct then it becomes extremely difficult to account for their origin, because in the ground substance, other than the nucleus and its karyosome, there appears to be no other structure and besides this fact there is no evidence for the belief that it arises as a differentiation process of the ground substance of the cell.

According to Klaatsch, the spots ultimately amalgamate with the intercellular meshwork, this coalescence Hase, Ussow and Paget did not observe. If Klaatsch's view be correct the white spots in the cells and the intercellular substance should take up the same stain with the silver impregnation. The intercellular network is stained brown, that is, like the product of secretion (Fig. 10). My preparations also show the same product stained brown round the nuclear membranes Fig. 11.

The polygonal layer of cells described above is (contrary to the view of Klaatsch) really the more distal layer on the ventral surface, reference, however, will be made to it again. In addition to this polygonal layer there is another more proximal layer to which no reference has been made before. This proximal layer is very closely adjacent to the scale (Fig. 9). As for the arrangement of the cells themselves, in these two layers throughout the series there is a great deal of variation in the appearance of the network of cells.

The distal cells-layer (polygonal layer of cells) on the ventral surface presents a very characteristic appearance. Figure 6 is a representation of the peculiar arrangement, which can be more clearly depicted than described. The entire scale layer is mapped out into several zones, which, as far as I have been able to make out, have no relation to the striation or to the growth of the scale itself. The most prominent region is the centre occupied by cells which are reticulate in nature, this region has more or less the appearance of a sponge, or of a honey-comb, with large cells each having a nucleus, this is surrounded by a zone of cells, which are slightly elongated and arranged in a concentric manner, followed by small rounded cells. This is next succeeded by a zone of prominent cells, constituting the largest portion of the scale. The cells are numerous and elongated radially, as these proceed outwards they become small and circular and are followed by a zone of cells near the periphery, which are elongated in a direction tangential to the scale and shorter in a direction radial to it; the last layer becomes gradually less distinct and is uninterruptedly continuous with the outer border of the upper margin. In some scales the early regions do not exist, and from the centre radiate the radial cells; these are followed by the usual cells. Besides these types

there are scales in which other arrangements prevail. The precise conditions under which these various arrangements come to exist I cannot state. It seems likely that they represent different stages in the activity of the cells. The proximal layer of cells on the ventral surface, which lies between the polygonal layer and the scale, has the appearance of an irregular network of large polygonal cells (Fig 9). The meshes vary in size, as does also the intercellular probably substance which becomes dilated and more prominent according to the quantity of the secretion accumulated in them. The nuclei in both the ventral layers are smaller and rounded, while those in the two dorsal layers are larger and greatly flattened. Besides these cells and their nuclei on the ventral surface, there are other nuclei which seem to be enclosed in several circular and irregular alveoli, giving the appearance of islets (Fig. 4). These nuclei are of varying size. They appear singly or in groups (fragmentation), showing no regular distribution, and appear to be in a special stage of activity. These nucleoli increase gradually in size and attain their maximum staining capacity. This is well seen on an application of Delafield haematoxylin, by which they acquire a beautiful blue tint.

Corresponding to the two layers of cells already described as lying on the ventral surface, there are two layers of polygonal cells at all stages of development of the scale on the dorsal surface (Figures 5 and 7). The difference between the layers of the two surfaces is that the intercellular material in the case of the dorsal cell layers is very poorly developed and the nuclei in these layers are much larger than entire cells in the previous stages.

### (c) *Connective tissue*

The great bulk of connective tissue constituted by the fibrous layer of the dermis is composed of bundles of connective tissue fibres, there being three sets of the latter, two sets running parallel to the surface diagonal to the long axis of the body, and the third set perpendicular to the other two sets. According to Hase the last set is really the diagonal fibres which have changed their direction. Paget believes them to be distinct, starting straight from the base of the fibrous layer without any previous horizontal course. I have followed the formation of fibres both in tiny embryos and in adult fish in preparations fixed with Fleming without acetic and stained with Orcein and Weigert's Resorcin Fuchsin stain, the fibres appear very distinctly, and I am able to corroborate both Hase's and Paget's descriptions. Sections stained by the above method show very distinctly that the fibres belong respectively to the collagen and the elastic type. The first two sets, running parallel and diagonal to the surface of the body, consist of wavy bundles, which very often change their direction and run perpendicular to the surface of the body. When these happen to

be cut at different levels, they appear to arise straight from the base; the cut ends of these fibres are met with at different levels. These fibres belong to the first type and I have no doubt that it is to them that both Hase and Paget refer. The elastic tissue fibres, which are characteristic in running in a straight course occur singly. They arise distinctly from the base and run quite perpendicular to the surface (Fig. 3).

In the scale pocket the connective tissue cells take the form of small rounded or stellate cells with processes which seem to anastomose among themselves; these cells form a firm support for the scale. During development, as the posterior end of the scale is being inclined outwards, the cells of the cutis between the epidermis and the scale enter on a stage of active cell proliferation. They make their entrance between the basal membrane and the scale, and become associated with the scleroblasts at the ends of the scale. These cells, from their appearance and mode of staining, closely resemble connective tissue cells which have detached themselves and taken up this position; the cells from the two sources in the region of the peripheral sections of the scale become so much intermingled that they are distinguished with difficulty. Klaatsch and Ussow, however, have seen cell clusters in the same position, and attribute to them the relief on the upper surface of the scale. Klaatsch says "At the same time there takes place an increase of dermis cells between the epidermis and the scales, and new elements thus become added to the scleroblasts on the upper surface of the scale, etc., etc. The scales thus become enveloped on all sides by loose connective tissue from which the scleroblasts receive new auxiliaries."

According to Hase, in the further course of the process of scale formation the transformation of cutis-cells into scleroblast takes place.

According to Paget, the papilla from its early origin acquires the form of a two-layered circular plate, between the upper and lower layers of which the scale makes its appearance. My observations support Paget's conclusions, but the scale papilla from its early origin is not two layered, but four-layered.

With regard to the connective tissue cells, it may be mentioned that they never take any part in the formation of the scale. The scale throughout its existence is so completely and symmetrically enveloped by the scleroblasts (Fig 6) that it would be wrong to imagine a break occurring in these layers

#### (d) *The development of the sclerites* \*

The sclerites make their appearance for the first time at the extreme out ends of the scale in both longitudinal and transverse

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\* On the dorsal surface of the scale are developed concentric inequalities which have been variously described as "lines," "ridges," "annuli," "sclerites," etc., etc.

sections and present slight elevations of a substance which to all appearance is very similar to that of the upper layer of the scale. The explanation of Klaatsch, Ussow and Paget with regard to their formation is essentially similar "The cells concerned arrange themselves so that they correspond exactly with the concentric ridges." In my preparations I find, firstly, that they occur at the extreme periphery (Figs. 7, 12), and appear to be laid down simultaneously with the other scale layers, and furthermore they arise within a cluster of cells. Just as the scale appears between scale papillae, so do also these appear between yet smaller cell aggregations, the sclerite papillae. In this smaller papillae the substance of the sclerite inclined towards the focus makes its appearance (Fig 7). The cells on the outer side of the ridge, situated as they are on the circumference of a widening circle, are scattered as growth proceeds and lie between the adjoining sclerites, the cells on the inner side are usually kept well in position.

It is well-known that the sclerites in some fish formed during the summer are wide apart, while those formed in winter are nearer together. The surface of the scale is thus mapped out into well-marked regions the summer and the winter bands. In other words, the scale denotes a well marked rhythm. These facts of development have been utilised for determining the age of the fish. It seems just possible that the width between adjacent sclerites is determined by mechanical causes. The sclerites are formed in response to the phasic activities of the scale-pocket cells and the interval between each of the phases is represented on the scale in the form of sclerites.

Each scale develops in a pocket of the skin the scale-pocket ("*Schuppen-Tasche*," Klaatsch). In the Trout, the limits of the scale-pocket are well defined and the scale with its close investment of four cell layers lies free of the scale-pocket.

During summer, owing to more active growth, the scale-pocket increases in size and makes a larger space available for the scale, so that the activity of the scleroblasts lead to an extension of the peripheral portions of the scale. The formation of the sclerites is capable of explanation on the hypothesis that the growth of the scale-pocket takes place at regular intervals, like the sclerites of the scale, they exhibit rhythm. After the growth of the scale pocket, there is a period of rest. At the next stage, the border of the scale abuts against the sides of the scale-pocket, as a result of extensive multiplication of cells on the ventral surface and enlargement of cells on the dorsal surface, there is an accumulation of cells at the borders of the scales on the dorsal surface. As no peripheral an extension is possible under these circumstances, the substance which builds up the sclerites accumulates between the cells, and takes the line of least resistance, in other words it takes a path of its own, subject to the restraints which are



imposed on it and the secretion accumulates in the interstices of the cells, which increase considerably in area by their own activity. At the completion of sclerite formation, the scale-pocket grows again, the strain upon the path of the scale being thus removed, growth takes the path of least resistance and the intermediate portions of the scale in between the sclerites come to be formed.

From this it follows that during summer, on account of environmental factors, the intervals of growth of the scale-pocket are long, leading to the formation of widely separated sclerites. In winter, for contrary reasons, the intervals of growth are greatly diminished, so that the sclerites, which come into existence, have not had enough time to be separated and are therefore crowded together. The sclerites denote the resting period, or they represent the arrested growth of the scale-pocket.

#### *Previous records and points of interest*

An important record in connection with scale development—and also one of the earliest—is that of Klaatsch (1890). He was the first to work out the details of the development, and the figures representing his various sections are very instructive. He based his opinion of scale formation and growth upon the presence of minute osseous bodies in the first layer of the scale and he regarded this part of the scale as built up of the ordinary bone tissue. He believed that the second layer of the scale is formed from the connective tissue which is developed from the scale-pocket. Paget (1920) contradicts the above conclusion—he believes that the upper layer of scleroblasts gives rise to the upper layer of the scale, and the lower scleroblasts to the lower layer. These facts are in agreement with my observations.

It now remains to review briefly some expressions of opinion on the following questions

- (a) Which of the two scale layers is laid down first?
- (b) Whether the covering epithelium is one cell thick or more?
- (c) The changes undergone by the dorsal scleroblasts.

(a) With regard to the first, Klaatsch and Ussow are of opinion that it is the upper layer of the scale which is laid down first. Klaatsch states, (regarding the relation of the lower to the upper layers), "it is of significance that the upper layer of the scale exists for a long time alone, and that it is not till later, when the covering of the scale has completed itself, that the outer part of the scale first appears. There exists indeed a genetic relationship between both layers, and the external body layer has actually occasioned the formation of the second.

An examination of entire scales from the very earliest stages shows that the lower scleroblastic cells are active at all stages of their existence. They very early assume the characteristic polygonal

form, and the white spots are also present ( Fig 4 ). If Paget's view, ( with which I agree ) that the upper scleroblasts give rise to the upper layer of the scale, and the lower scleroblasts to the lower layer, be correct, then undoubtedly the lower scale layer exists at all stages. The polygonal layer of cells, which Klaatsch and Ussow take such pains to describe as lying over the scale, lies really below it. Attention was drawn to this fact by Paget and I can fully confirm his observations. To the activity of this layer they attribute the formation of the upper scale layer. In the light of these observations, it would seem that both Klaatsch and Ussow make contradictory statements, viz, the formation of the upper scale layer first and associated with it the lower active epithelium, in their view, the upper. The study of preparations stained with Delafield's haematoxylin corroborates this statement.

I know of no method of determining which of the layers is deposited first. The microscopic indications support Paget's statement that the two are laid down simultaneously. In the Cod, Tims ( 1902 ) showed that the inner layer which forms the fibrous plate develops first and on this the sclerites subsequently differentiate themselves.

(b) The question here to be decided is whether the covering epithelium is one cell thick or more.

In connection with the cell layers different accounts exist, this is due to the fact that the Delafield's method of preparation obliterated the cytoplasmic outlines and made the limiting membranes invisible, ( compare Fig. 14 with Figs 5 and 9 ) and therefore both on the dorsal and on the ventral surfaces the double nature of the cell-layers was not clear. These layers in fact are capable of being lifted up and separated. Klaatsch, however, described several layers. He says that the cell structure on the external surface of the scale show differentiation into several layers of cells, and that these cells build up the substance of the first layer of the scale. In the opinion of Hase and Paget, the covering epithelium is only one cell thick.

If a reference is made to my figures the question is very convincingly answered. In preparations of scales mounted entire and stained by the special method, the four cell layers lying in different focal planes can easily be demonstrated, and the scale throughout life remains enclosed by these.

(c) The changes undergone by the dorsal scleroblasts described by Klaatsch, Ussow, and Paget are not clear to me.

According to Ussow, the cells which lie over the already secreted substance of the first layer of the scale use themselves up in the formation of the scale material ( its first layer ) much more rapidly than those of the under layer, in later stages consequently one finds only nuclei without any trace of plasma.

Paget, in describing the striations, makes the following statements. "When the striae are once formed, practically no further growth takes place and the nuclei of the cells appear not to attach themselves so closely to it as at first, nevertheless, the whole of the plasma is used up in the process of stria formation" (Fig. 14.)

A study of preparations impregnated with silver makes it clear that the dorsally placed cells, which appeared to possess no cell-walls, have perfectly distinct cell limits like those on the ventral surface (Fig 5). It is also apparent that the protoplasm is not used up in the building up of the scale, but on the contrary some product is separated from the cells and contributes to the formation of the scale. An interesting question arises with regard to the behaviour of the dorsal scleroblasts. Why do the cell limits on the dorsal surface of the scale not take up the same Delafield's stain which the ventral cells do readily? One explanation is that the fixing reagents, which were employed in the histological technique, destroyed these cell outlines.

Another explanation would be to regard the ventrally placed cells as young (meristem in plants), with plenty of protoplasm which readily takes up the stain, the ventral marginal cells as they pass on to the dorsal layer at the margins are no doubt older in history. These latter become in a sense static. The protoplasm becomes miscible with the ground substance with the result that ordinary methods of staining will not bring up the cell walls. By silver impregnation the colouring matter is deposited in the intercellular regions in the form of a precipitate, making the cell limits more opaque. In plants a similar phenomenon exists. In the meristematic cells, the cytoplasm occupies the whole volume of the cell and stains with the usual reagents. When the cells become old, the nucleus lies in a space surrounded by a thin film of cytoplasm connected by a number of strands with the cell-wall. In these cases the cell-wall takes up the stain because of the presence of cellulose in the cell-wall, the absence of which would make it just as difficult as appears to be the case in animal cells.

The cell membrane is to be regarded as part of the protoplasm itself, and it varies in its composition according to the chemical processes going on in the cell.

#### SUMMARY.

(1) A satisfactory technique for the investigation of developing teleostean scales has been described.

(2) The process of separation of the hard structure of the scale (upper and lower layers) is the work of four layers of cells, to which the term scleroblasts may be applied; these envelop the scale symmetrically throughout life.

(3) The upper scleroblasts have, throughout life, definite cell limits and become just as clearly polygonal as the lower scleroblasts.

(4) The upper scleroblasts give rise to the upper scale layer, the lower scleroblasts to the lower scale layer as well as to the upper scleroblasts themselves.

(5) The protoplasm and cell limits persist throughout life, the substance which builds up the scale arising as an intercellular secretion.

(6). The scale is situated in a special scale-pocket formed of connective tissue.

(7) The sclerites arise at the extreme peripheral ends of the scale and are formed by groups of cells

(8) It is suggested that the form assumed by the scale and the development of the sclerites is due to intermittent growth of the scale pocket and to the several tensions and pressures to which the scale is subjected during growth.

#### EXPLANATION OF PLATES

All the Photo-micrographs were taken under a Watson's microscope provided with Apochromatic objectives and Watson's Photo-micrographic apparatus

FIGURE 1 Trans. section through the skin of young Trout,  
1/6" objective x 4 ocular

- Showing (a) Formation of dermal scale papillae,  
(b) Differentiation of the dermis into an inner fibrous and an outer spongy layer.  
(c) Musculature  
Trout 3.5 cms. long.

FIGURE 2. Trans. section through the skin of young Trout,  
1/6" objective x 4 ocular

- (a) Epidermis with mucous cells,  
(b) Cuticularised lower borders of the basal epidermal cells,  
(c) A definite basement membrane,  
Trout 2.5 cms. long.

FIGURE 3. Longitudinal vertical section of skin of Trout to show relation of fibres. Weigart's Resorcin. Fuchsin stain.

1/12" objective x 4 ocular.

- (a) Collagen fibres running in bundles and showing a change in their direction,  
(b) Elastic fibres arising straight from the base and running singly.

**FIGURE 4.** A part of scale of Trout. Surface view of the ventral surface. Stained Delafield's Haematoxylin.  $1/6''$  objective x 4 ocular.

- (a) Large polygonal cells which exhibit every variety of shape
- (b) White intercellular spaces between the cells.
- (c) Whitish rings surrounding the nucleus The white spots are massed to one side of the nucleus and in some cells separated from it.
- (d) Excessive nuclear fragmentation.

**FIGURE 5.** Part of scale from the dorsal surface. ( Nitrate of Silver preparation ).  $1/6''$  objective x 4 ocular. 2 layers of scleroblastic cells. Impossible to demonstrate without the silver method of staining

**FIGURE 6.** Part of scale, stained with Delafield's and Eosin.  $2/3''$  objective x 4 ocular. Showing general relation of distal ventral layer of cells.

**FIGURE 7.** One end of the scale in section.  $1/12''$  objective x 4 ocular Relation of scleroblasts to the scale.

- (a) Cluster of cells at the cut ends where a ridge is in process of formation.
- (b) Also characteristic arrangement of cells which form the ridge.
- (c) Note whitish spots in nuclei.

**FIGURE 8.** Transverse section of scale with several layers of scleroblasts on the outer surface.  $1/6''$  objective x 4 ocular.

- (a) The more proximal cells attached intimately to the scale.
- (b) The lower cells have separated away from the scale and appear more markedly flattened than those of the upper layer.

Trout 3 5. cms. long.

**FIGURE 9.** Part of scale Surface view of ventral cells from the anterior region. (Nitrate of Silver preparation).  $1/6''$  objective x 4 ocular.

- (a) Two layers of scleroblastic cells.
- (b) The layer of cells ( proximal ) attached to the scale has very large spaces.

- FIGURE 10.** Part of scale. Surface view of the ventral surface, only one layer in focus. (Nitrate of Silver preparation).  
 $1/6''$  objective x 4 ocular.  
 (a) Intercellular substance as well as the diffused secretion stained brown.
- FIGURE 11.** Part of scale. Surface view of the ventral surface. (Nitrate of Silver preparation)  
 $1/12''$  objective x 4 ocular  
 (a) The substance massed to the nucleus stained brown.
- FIGURE 12.** End of scale in long vert section.  
 $1/12''$  objective x 4 ocular.  
 (a) The formation of the ridge at the extreme end  
 (b) The upper homogeneous layer of the scale raised into ridges  
 (c) The stratification in the lower lamellar layer just visible
- FIGURE 13.** Transverse section of scale.  
 $1/6''$  objective x 4 ocular.  
 (a) Position and relation of scleroblasts of the two surfaces at the end.  
 (b) Cuticle bordering the cells
- FIGURE 14.** Part of scale from the dorsal surface (Delafield's Haematoxylin preparation) Compare with Figure 5.
- FIGURE 15** Transverse section of scale.  
 (a) Cluster of connective tissue cells at the end.

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Fig 1

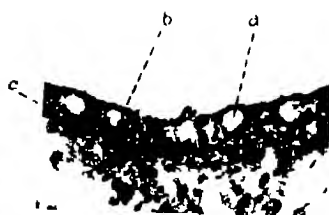


Fig 2

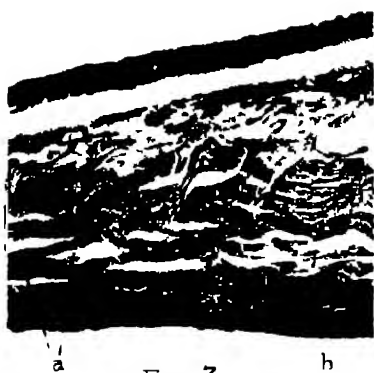


Fig 3



Fig 4







Fig 14



Fig 15



# ON THE PHASICAL MORPHOLOGY OF THE THYMUS GLAND IN SOME COMMON EUROPEAN FISHES AND IN TWO CYCLOSTOMES.

By

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( with 6 text-figures and 1 plate )

CONTENTS Introduction—Material—The Thymus in the Teleosts  
—The Thymus in the Elasmobranchs—The Thymus in two Cyclostomes—Conclusions—References

## INTRODUCTION.

The present paper on the Phasical Morphology of the Thymus Gland in some Common European Fishes and in two Cyclostomes is based on the work done by me in the Oceanography Department of the University of Liverpool at Liverpool, while working on the Phasical History of the Thymus Gland in Place of Various Ages, etc., already published in the fifth part of the first volume of this Journal. As indicated in the title of this paper, this survey is not complete and requires to be supplemented by an examination of the thymus gland in some more fishes, particularly specialized ones. The work is being continued by me in the Zoology Department of the Royal Institute of Science, Bombay, and its results will be published in due course.

## MATERIAL

This investigation was carried on mostly with material fixed in formalin. The specimens were well preserved and in sections produced satisfactory results when stained with Mayer's Glychaemalum.

## THE THYMUS IN THE TELEOSTS

### *Pleuronectes limanda*

( Specimen 24 cms long. )

The thymus in this specimen was in position and shape similar to that of the plaice which has been described in detail in my paper thereon already published in this Journal. It was 5 mm long, 2 mm broad and 1 mm thick. It consisted of a few rounded and rod shaped lobules loosely packed together. On its upper surface it consisted of two rows of lobules.

In another specimen 29 cms. long it was 6.5 mm long and 2 mm. broad. Thus in both of these it was evidently smaller than the thymus in the plaice of the same length.

in length, 7 mm. in breadth and 15 mm thick in the middle. As it was applied to the curved external surface of the auditory capsule, it appeared less broad than it really was, when its outline was projected to a single vertical plane.

In connection with its histology much could not be observed in a series of 20 $\mu$  sections of a specimen preserved in 3% Formalin. Still it was noticed that there were no coagulum balls. Its external margin was in contact with a thin layer of branchial epidermis and its internal margin was not definite. Moreover numerous thymus cells were seen in the adjoining connective tissue all along its internal margin.

The pronephros was behind the thymus by as much as the thymus was behind the eye. Lymphocytes were accumulating in it.

In a young herring 4.5 cm long from the same locality, the thymus measured 2.2 mm long, 1.9 mm broad and 6 mm thick in the middle. Thus during this time it had trebled its former length and thickness while its increase in breadth was relatively less. Now it nearly reached the head kidney. Its internal margin was quite definite except in the middle. In the connective tissue adjoining this central part a large number of thymus cells were seen. Along its external surface underlying the epidermis a clearer area could be distinguished. It was 0.6 mm thick or in other words one-tenth of its whole thickness. It contained relatively a less number of thymus cells and the interspaces were larger. Irregular clearer spaces and pycnotic thymus cells were seen scattered throughout the thymus.

In a young herring 12 cm long and less than two winters old the thymus measured 5 mm. long and 2 mm broad. It appeared to be pushed out towards the epidermis by the underlying muscle and it appeared as a small ingrowth of the epidermis in that region. It clearly showed that its growth was not keeping pace with the growth of the body even before the fish became mature.

#### *Clupea sprattus*

In a specimen 7.5 cm. long and three years old the thymus had completely disappeared. Its place was occupied by fibrous connective tissue.

#### *Salmo fario.*

Deanesly has recently studied the life history of the thymus in this fish. It resembles the life history of the thymus in Herring. Sections were cut of a newly hatched larva of this fish and it was observed that the thyroid was also rudimentary as the thymus.

#### *Centrolophus niger*

(Specimen 52 cm. long.)

In this deep sea form the thymus was altogether absent. While searching for the thymus the lymphoid tissue of the head kidney was

easily reached as the intervening connective tissue was very loose. The head kidney looked like the thymus but in sections its true nature was revealed. Hammar has recorded the thymus in a specimen of *Centronotus gunnellus* 12.5 cm long.

#### THE THYMUS IN ELASMOBRANCHS.

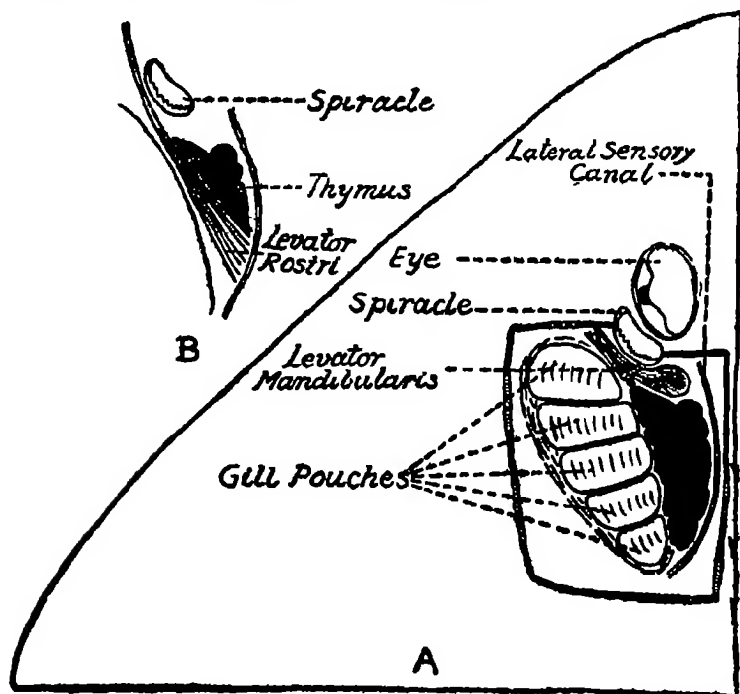
##### *Chimaera monstrosa*.

In a specimen 70 cm. long it was found to be absent. But Hammar has recorded it in this species and he has stated that the process of involution begins in specimens of about 75 cm. length.

##### *Raja maculata*.

(Specimen 18 cm. across the body ) Text-Fig 3

The thymus of each side was situated in this specimen on its dorsal side behind the spiracle and on the mesial side of the gill pouches. When the integument in this region was removed a layer



TEXT FIG 3

Thymus of *Raja maculata*. A, Dissection of 18 cm. wide specimen exposing the thymus on the left side. B, Part of the thymus exposed on removing the skin and connective tissue.

of about 15 ampullary tubules was seen lying in the underlying loose connective tissue. When the tubules were removed a part of the thymus

was exposed between the lateral sensory canal and the gill pouches. The remaining part along the gill-pouches was covered by a paddle-shaped muscle whose tendon passed straight to the anterior margin of the snout by the outer side of the spiracle. When this muscle was removed the roughly triangular dorsal surface of the thymus was fully seen. Its outline was modified so as to fill in the space among the surrounding organs. On its mesial side it closely followed the sigmoid curve of the lateral sensory canal and on its external side it pushed its way between the gill-pouches. Between its anterior side and the spiracle was seen the stout levator mandibularis muscle. When it was separated from the surrounding parts it was seen tapering to an edge on the ventral side. It thus roughly resembles an elongated prism. All along its surface it consisted of rounded lobules closely packed together.

When the connective tissue enclosing it was removed it was seen to be made of five lobes. These lobes corresponded to the gill-pouches but their margins alternated with the margins of the pouches.

It was 19 mm long and 7.5 mm broad. In a specimen 26.5 cm. across the body the thymus was 16 mm long and 7 mm broad.

In a specimen 34 cm. across the body the thymus was so well developed that its dorsal surface, instead of being flat as before, now bulged out between the lateral sensory canal and the rostral levator muscle. The latter now occupied a trough between the thymus and the gill-pouches. The thymus was 22.5 mm long and 10.5 mm broad.

#### *Rasa clavata.*

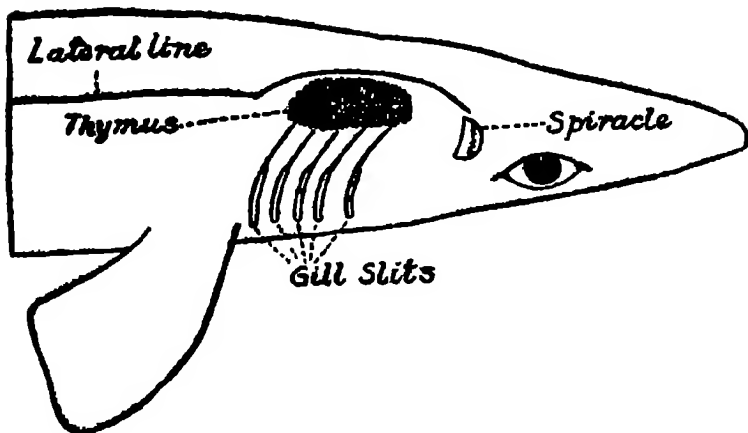
In this fish the thymus occupies the same position and has the same shape as that in the former ray. In a specimen 9 cm. across the disc it was 8 mm long and 3.5 mm broad. In a specimen 20 cm. across the body it measured 11 mm long and 5 mm. broad, and in a specimen 49 cm. across the body it was 28 mm long and 18 mm. broad. The connective tissue covering it was fibrous and the levator rostri muscle was shifted towards the gill-pouches. It appeared to be proliferating at the edge but its microscopic study showed that it was really involuting.

#### *Acanthias vulgaris.*

(Specimen a foetus 19 cm. long.)

The foetus had a yolk-sac, as large as itself, attached to it. Its thymus (Text-Fig 4) was situated on each side immediately below the lateral line in the region of the gill-slits. When the skin was removed it presented an ellipsoid area made of numerous small lobules. Some of the lobules were elongated but most of them were rounded. They appeared to be arranged in parallel rows running between the lateral line and the gill-slits. It measured 11.5 mm. long and 4.5 mm.

broad. It was comparatively very thin as it consisted of a single layer of the lobules



TEXT FIG. 4

Lateral view of a foetal *Acanthias vulgaris* 19 cms. long showing the thymus on the left side

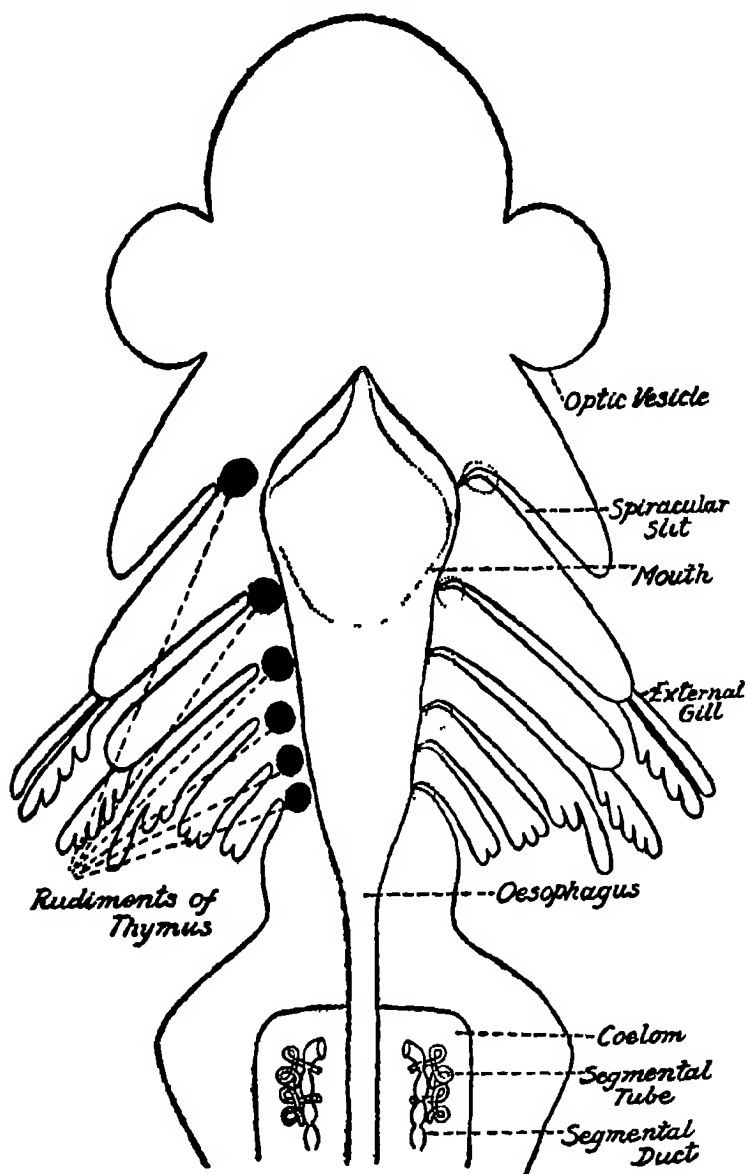
In a foetus 21 mm. long (Text-Fig 5) the thymus was represented by six rudiments on each side at the dorsal ends of the gill slits. The foetus was very young as its eyes were represented by optic vesicles seen as lateral outgrowths in front of the spiracle or the most anterior gill-slit. The fore-brain bulged out ventrally between the optic vesicles. On account of the cranial flexure the mid brain formed the anterior end of the long axis of the foetus. The mouth was a deep diamond-shaped pit behind the fore-brain. Filaments of external gills were seen coming out of all the five gill slits. The pectoral and pelvic fins were represented by tiny lateral flaps.

In Text-Fig. 5 the positions of the thymus rudiments are shown in the dorsal view of the foetus. Their outlines were reconstructed from a series of 20 $\mu$ . transverse sections. The first thymus rudiment on each side was in connection with the dorsal edge of the spiracle and was situated midway between its external and internal openings. It was like an elliptical plate thickened in the middle. It partly covered the dorsal edge of the spiracular slit and chiefly spread down its posterior wall. In a longitudinal section of a foetus passing through it, it was like the root-cap seen in a longitudinal section of a root tip. In sections the area of the thymus rudiment was marked by the absence of the basal membrane between the hypoblastic epithelium and the surrounding connective tissue. Moreover the thymus rudiment (Plate I, Fig 1) or the part of the epithelium was thickened and consisted of rounded, loosely packed cells unlike the columnar closely packed cells of the surrounding epithelium. In sections the surrounding epithelium was



seen to have thickened but it may have been due to the sections being not quite transverse to it.

In a specimen 70 cm. long the thymus was quite vestigial.

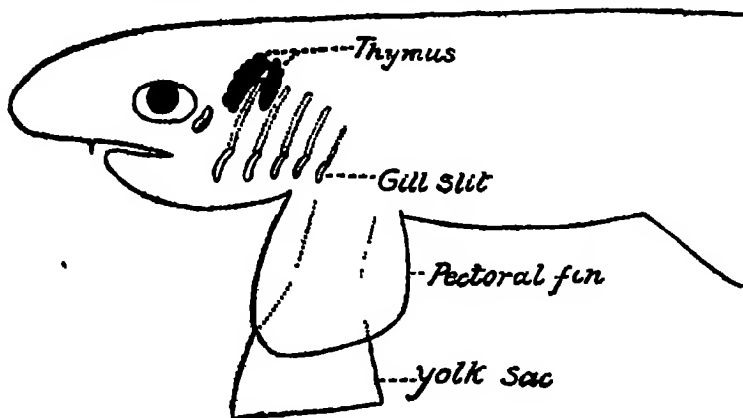


TEXT FIG. 5

Dorsal view of a foetal *Acanthias vulgaris* 22 mm. long with the thymus rudiments and the primitive kidney shown in their places.

*Scyllium canicula.*

In an embryo 8 cm long (Text-Fig 6) the thymus was well developed and consisted of two lobes lying dorsal and just anterior to the



TEXT FIG 6

Lateral view of an embryonic Dogfish 8 cm. long showing the thymus. first two branchial arches respectively. The first lobe was larger and longer than the second. Both of them were very close to each other at the dorsal end. Each of them consisted of a few lobules.

In a dogfish about 70 cm long the thymus was quite inconspicuous. When it was sectioned with its surrounding connective tissue it was found to be reduced to a few minute lobules from which a large number of thymus cells had emigrated and left vacant spaces behind.

## THE THYMUS IN TWO CYCLOSTOMES.

*Lampetra fluviatilis*

(Specimen a larva 6.5 cm. long.)

This specimen preserved in methylated spirit was secured from the British Museum (Nat. Hist.) through the courtesy of Dr J. R. Norman. In this specimen (Plate I, fig 2) the thymus was represented by a pair of irregular nodules of the thymus cells situated in the neighbourhood of each of the external branchial pores. One of them was dorsal and the other was ventral to the latter. Immediately external to the nodule there is a large blood sinus and the thymus cells appear to form a part of the contents of the blood sinus. But a good differentiation was obtained by staining the sections with Glycamaalum, which proved their distinctiveness. As this series of sections was not complete the number of such nodules forming the thymus rudiments could not be determined. But Schaffer has stated that all branchial pores have similar pairs of nodules and therefore the thymus in the larva of this Lamprey consists of twenty-eight nodules.

In a Brook Lamprey (*Lampetra planeri*), 75 cm. long the thymus was absent.

#### CONCLUSIONS.

The present survey of the thymus gland of fishes deals with species representing the large morphological divisions of fishes. Thus it includes notes on the thymus of some of the round bodied and flattened bony fishes, some Rays and Dogfishes, a Holocephalian and two Cyclostomes. It also includes a reference to a deep-sea form. From the condition of the thymus observed in various fishes at various stages of their life histories it is evident that the organ is present in all fishes but that the organ has a variable origin and a variable duration in different kinds of fish. While in the Rays the thymus rudiments are seen in connection with all the five gill pouches, in some Dogfishes it is confined to the first two gill-pouches only. Similarly while the thymus is completely reduced at or before the time of maturity in Herring and Trout, it continues to grow in Rays and Flat fishes, and also in Cod. This suggests that no correlation could be established between the involution of the thymus and the maturity of the gonads in fish. It further suggests that in some fishes like Rays and Flat-fishes the thymus continues to be active and functional beyond the time of their maturity.

When the size of the thymus in various fishes is considered it strikes one that the organ in flattened and sluggish fishes like the rays and flat-fishes is more developed than in the round-bodied and active fishes.

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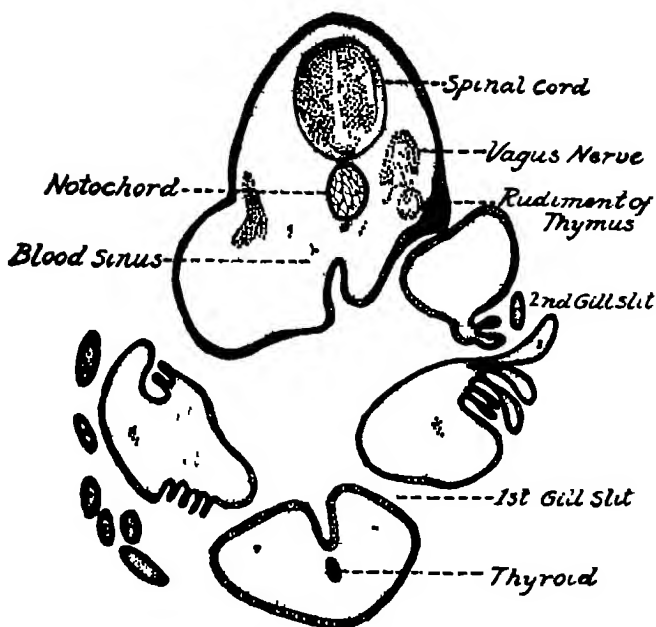


PLATE I, FIG 1

Transverse section of a foetal *Acanthias vulgaris* 21 mm long, passing through the thymus rudiment of the third gill-slit

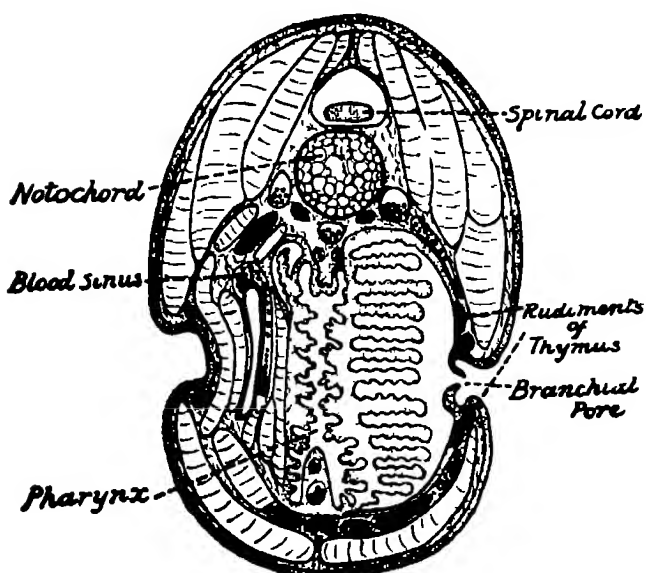


PLATE I, FIG 2

Transverse section of a larval *Lamperta fluviatilis* 6.5 cms. long, passing through a branchial pore on one side



# STUDIES ON THE HONEY BEE, *APIS INDICA*—I

By

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( 4 Text-figures and 4 Photographs )

## *Introduction and Historical Background.*

A study of the indigenous honey bees has been undertaken at the suggestion of Professor C. J. George, and though the work will take many years for completion, I have no hesitation to publish the following few observations in view of the interest they will create in Apiculture in the Bombay Presidency. I take this opportunity to record my indebtedness to Dr. George for offering me his valuable guidance in pursuing this study.

Apiculture as a side line industry to Agriculture is practised in many countries. In some of these countries the industry is carried out on a large scale. Figures are not available on the output of honey for all these countries, but it is well-known that thousands of tons of honey are exported by Canada, Australia and the United States of America. Though the possibilities of apiculture in India have received the attention of Government as early as 1883 when, as a result of an enquiry, the Government of India published the replies from local Governments under the title "A Collection of Papers on Bee-keeping in India", the industry is still in an infant state in India. One of the early attempts at culturing bees on scientific lines was made by the Agricultural Research Institute, Pusa. In 1910 and 1911 the Institute imported some colonies of the European bee. Later Mr. T Bainbrigge Fletcher, Imperial Entomologist, published two articles on bee-keeping in the Agricultural Journal of India, Vol VI, Part IV. A further consolidated account came out in 1914 as Bulletin No. 46 of the Agricultural Research Institute.

During the years 1911-1916 Father Newton, S. J., conducted trials on the cultivation of the Indian bee *Apis indica*. His results were published in an article in the Agricultural Journal of India, 1917. The Department of Agriculture, Mysore, began the study of apiculture with the Indian bee about ten years ago and have made good progress. Mr. J. S. Baldry attempted culture of the Indian bee at Narsapur during 1926-1929. The account of his experience was published in the "Illustrated Weekly of India", dated 7th December 1930, 28th December 1930, 15th February 1931, and 22nd November 1931,

Recently the Rural Reconstruction Branch of the South Indian Y. M. C. A. has taken up apiculture (culture of *Apis indica*) with a view to popularize it among the Indian farmers. They have their centres at Coimbatore, which is subsidized by the District Board, and at Marthandam (Travancore). The cultivation of the Indian bee has also been attempted at the Agricultural College and Research Institute, Coimbatore.

*Outline of the Habits of the Indigenous Species of Apis.*

There are three species of *Apis* in India,—*Apis dorsata*, *Apis indica* and *Apis florea*. In some of their habits the three species resemble a good deal, though the comb building and nesting habits are very different.

*Apis dorsata* (Fig. 1) is the biggest of the three and is primarily a dweller of the forest. The Western Ghats afford ample favourable

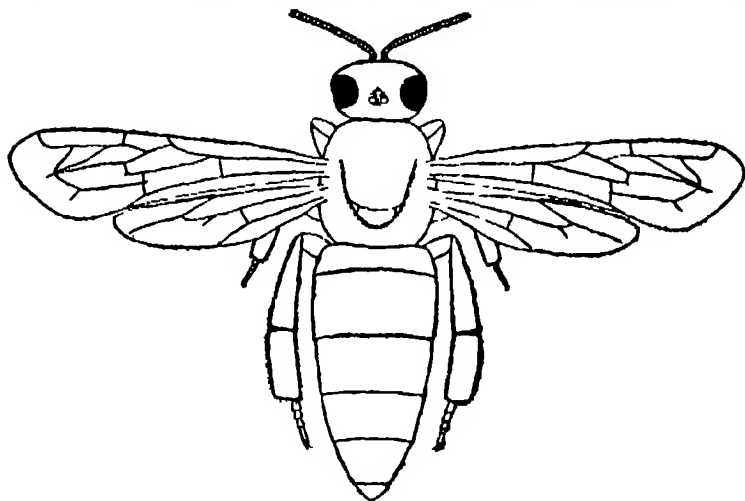


Fig. 1 *Apis dorsata* Fabr (worker)  $\times 3.3$ .

ground for it. It is usually known as the "rock bee", and builds its hive on high situations, and the shelter from an overhanging cliff is a very favourite haunt for it. It always keeps its nest a certain height or more from the ground, thirty feet being the lowest noted so far in this part of the country. Each colony has only a single enormous comb. The average size of a comb is about  $18'' \times 18''$ , though combs of  $39'' \times 18''$  are on record (Gosh—Rept Third Ent. Meet., Pusa, 1919). The cell measures roughly  $\frac{1}{2}$  of an inch in diameter and is  $\frac{1}{10}$  of an inch in depth. The bee is very efficient on the wings and can fly upto 300 yards at a stretch. Its long abdomen acting like a rudder adds to the efficiency of flight. When irritated it is ferocious and animals and human beings dread it,

It is believed that *Apis dorsata* has a migratory habit, living in the hills during the Summer and migrating to the plains in the rainy season. This record under careful scrutiny does not seem to be authenticated. A hive of this insect has been in existence under the eaves of the Wilson College continuously for the last two years. A second swarm which settled early in June last is still continuing in Bombay though the Summer has set in. The belief also proves unreliable when we analyse the conditions absolutely essential for such a migration. In the first place it must be credited with the power of anticipating the coming change of weather. There are no grounds to make such an assumption. Further the workers and the queen will have to fly a long distance in order to reach either destination, and even a six-months old queen will be unable with her heavy abdomen to accomplish that feat.

*Apis florea* (Fig 2) the smallest of the three species, builds its nest at lower heights than does *Apis dorsata*, but like the latter it builds

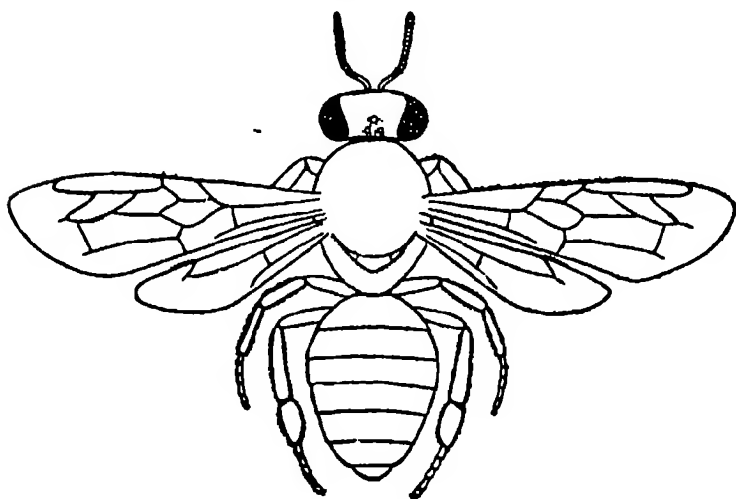


Fig. 2. *Apis florea* Fabr (worker) x 66

single combs. Its comb does not measure more than 6" x 6" Each cell is only  $\frac{1}{16}$  of an inch in diameter and  $\frac{3}{10}$  of an inch in depth, or just half that of *Apis dorsata*. It is a poor honey gatherer but its honey has a fine taste. It is a poor flier, much less efficient than *Apis dorsata* and *Apis indica*. It has been found that it is subjected to attacks by a mite.

*Apis indica* (Fig. 3) is intermediate in size between *Apis dorsata* and *Apis florea*. It builds its hive at lower heights than *Apis dorsata*. It inhabits hollows or crevices on trees, walls or some masonry constructions. Like *Apis mellifica*, the European species, it builds parallel combs and is therefore thoroughly suited for domestication. It



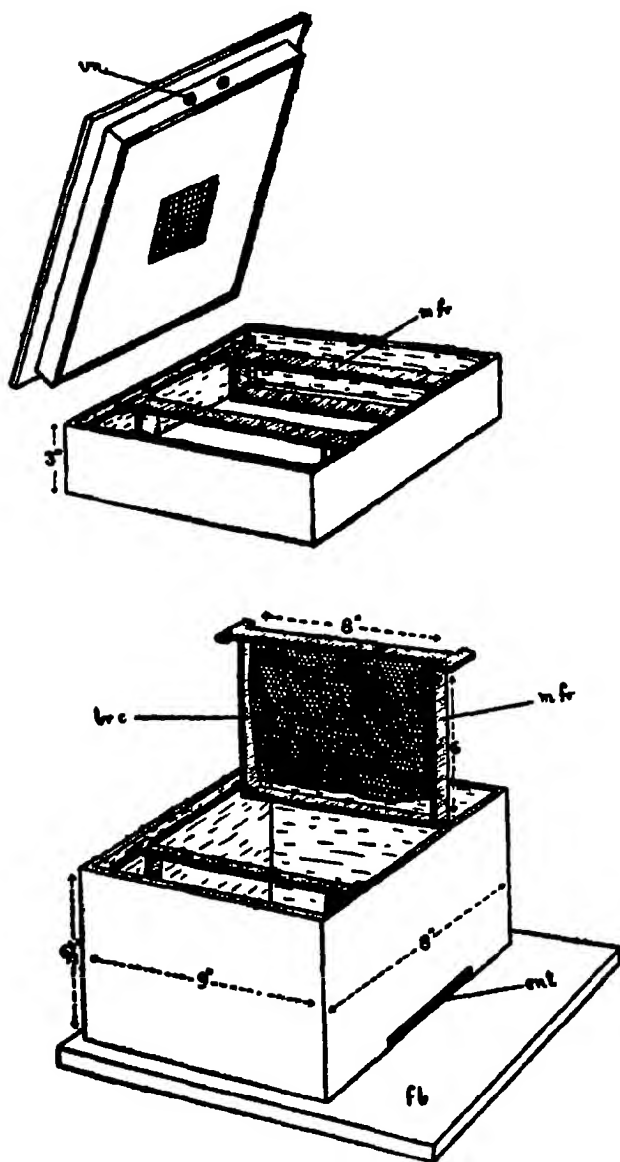


Fig 4. An artificial box hive, ( detached )

A.—The basal piece showing only two of the seven moveable frames. m. fr, moveable frame. br c., brood comb f. b., foot board. ent, entrance to the hive.

B.—The middle piece showing only two of the seven frames. m. fr , moveable frame.

C —The top piece with its ventilations. vn., ventilation



1



2



3



4

# STUDIES ON *APIS INDICA*

## EXPLANATION OF THE PLATE.

- Photograph 1 An experimental bee hive kept in the Hanging Gardens, Bombay
- Photograph 2 The three pieces of the artificial hive
- Photograph 3 One of the moveable frames, with brood comb, pulled out of the hive
- Photograph 4 A typical comb of *Apis indica*, with the workers



the hive and bears on its walls small round openings (7%) closed with wire nets for aeration. The wire netting prevents the bees from passing through the opening at the same time offering sufficient ventilation. A hive of this kind could be made for Rs. 5/.

On all the moveable parallel frames the bees construct readily their wax combs. The larger lower combs (Fig. 4 A. *br. c.*) are utilized as brood combs with their supply of brood honey and pollen, while the smaller upper combs are used for the storage of surplus honey.

# THE CHROMOSOMES OF POECILOCERA PICTA, FABR.

(A short-horned grasshopper)

By

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## *Introduction.*

Since the beginning of this century male germ cells of Orthoptera, particularly of the short-horned grasshoppers, Acrididae, have furnished very favourable material for chromosomal studies. In Acrididae more than in any other group of insects it has been demonstrated by a host of investigators among whom Dr. McClung ('14) and his associates have been most active that a remarkable constancy of numbers, forms, size and behaviour exists in the chromosomes of a very large number of representatives of this family of short-horned grasshoppers.

Since 1928 one of us, Asana ('28, '30, '31), has been observing a remarkable deviation in chromosome numbers in some representatives of Indian grasshoppers of the sub-family Pyrgomorphinae of the family Acrididae, and a preliminary account of the chromosomes of an Indian species *Poecilocera picta* is presented herewith.

## *Material and Method.*

The following observations are based on testes derived from nymphs in all stages and adults of *P. picta* collected from the fields adjoining the Gujarat College, Ahmedabad. Large numbers of these insects are found feeding on the leaves of *Calotropis* and the common hedge plant, *Euphorbia*, late in the monsoon. The youngest nymphs appear in the field two times in a year, once in April, and again in October or early November.

Specimens were decapitated or killed by pouring a little xylol on them soon after they were obtained from the field, testes quickly dissected out and subjected to a variety of fixatives, of which Champy's mixture, weak Flemming with reduced glacial acetic acid or just a trace of acetic, and Benda's fluid seemed to be the most favourable for chromosome studies. Sections were cut 10 to 15 micra thick and stained with Heidenhain's iron haematoxylin.

## OBSERVATIONS.

1. *Spermatogonia* The chromosomes of the spermatogonial metaphase are all rod-shaped, straight or slightly curved (Fig. 1). They arrange themselves radially in the equatorial plate, forming a typical rosette. In sections from well preserved material the homologous mates are easily recognized. The diploid number of chromosomes as seen in the spermatogonia of this species is 19, 9 pairs of which are to be regarded as autosomes, the remaining one is the X-chromosome or the accessory chromosome functioning as a sex determinant. This unpaired accessory can be easily recognized by its rough contour, and it is rather narrower than the autosomes.

According to McClung ('14) the diploid number of chromosomes in several numbers of Orthoptera belonging to the so called Hippicus-type appears to be 23. While 19 chromosomes as the diploid number have been reported in a few species only, for instance, in *Atractomorpha* (Machida, '17) and *Pamphagus* (Granata, '10). As compared with those of the Hippicus type, the chromosomal complex as seen in *Poecilocera*, *Atractomorpha* and one or two other species is devoid of 4 dot-like chromosomes.

2. *Primary spermatocytes* The chromosomes of the primary spermatocyte metaphase at the first maturation division (S. C.), are 10 in number which are composed of 8 ring-tetrads, 1 rod-tetrad and an accessory or a sex chromosome (Figs. 2-3). The accessory is always situated in the central part of the equatorial plate surrounded by other chromosomes. In this reduction division the autosome tetrads are all divided into two equal halves, each half assuming a V-shape, while the sex chromosome goes undivided to one of the two poles of the spindle slightly in advance of the batch of the V shaped halves going to the pole towards which the accessory proceeds, as is shown in the tangential view of the spindle (Fig. 4).

3. *Secondary spermatocytes at the metaphase* As a result of the asymmetrical first maturation division as seen in the above-mentioned primary spermatocytes two kinds of secondary spermatocytes appear at the metaphase of the second maturation division (Figs. 5-6). One group consists of what may be called X-class secondary spermatocytes each of which contains the accessory or sex chromosome besides 9 autosomes, thus having in all 10 chromosomes. In the other group of secondary spermatocytes the accessory or X-chromosome is absent. Cells of this second group contain only 9 autosomes. The chromosomes as seen in this second maturation division are all V-shaped at the metaphase, each V-shaped chromosome consisting of two rods superimposed at their inner ends where the spindle fibres are attached.

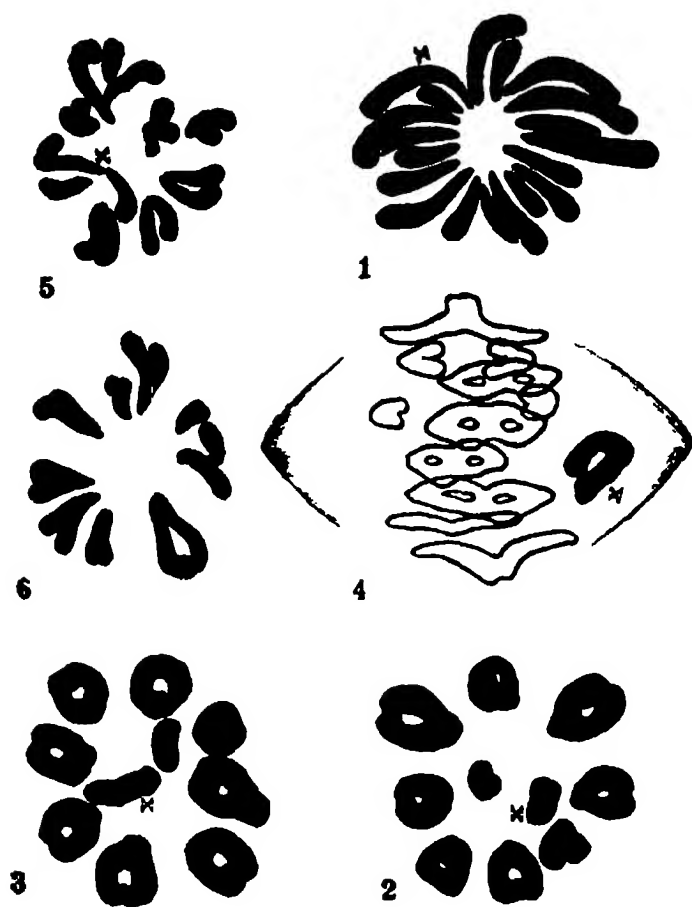
Throughout these two maturation divisions the accessory chromo-

some shows a characteristic feature in that it does not get as intensely stained by the dye as the autosomes; it shows comparatively diffuse staining.

We are greatly indebted to Prof. Dr. Kan Oguma to whom we wish to express our sincere appreciation for his great interest and helpful criticism in this study.

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*Puccinopsylla picta* (2,000 X)

1, spermatogonial metaphase, 14 chromosomes, 2-3, primary spermatocyte metaphases, 10 tetrads, 4, side view of first division, 5, secondary spermatocyte metaphase, X-class, 10 dyads, 6, the same, no X-class, 9 dyads X, the sex chromosome





# THE PROTRUSIBLE VESICLES IN CYRTACANTHA CRINAE ACRIDIINAE ( Orthoptera )

By

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## INTRODUCTION

The writer discovered these vesicles for the first time in 1929 in *Anacridium aegyptium*. Anatomical studies since then on other Acridinae have shown that the vesicles are present in all the specimens

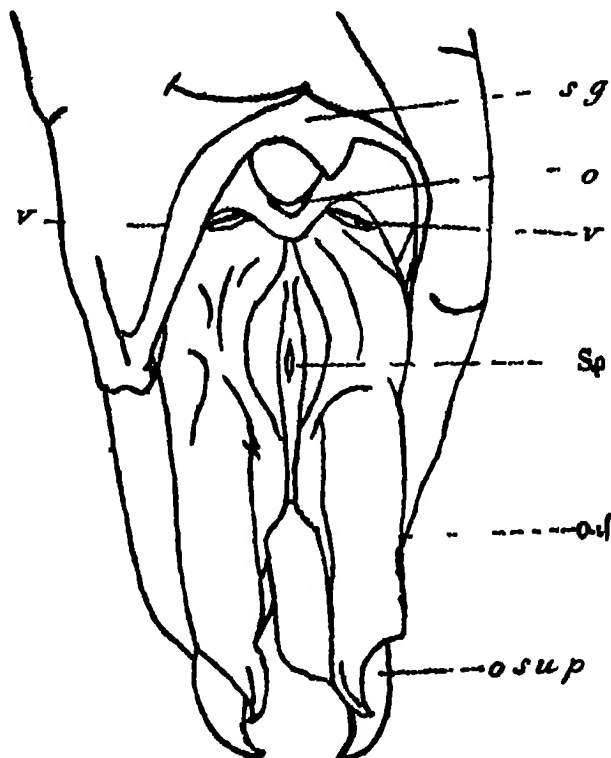


Fig 1 The posterior end of the abdomen of *Anacridium aegyptium*, female seen from the ventral aspect the sub-genital plate lifted up and the body tilted to one side to show the orifices of the vesicles (V) and that of gonopore (O) S p.=the opening of spermatheca s. g.=sub genital plate o i=ventral valves of ovipositors, o. sup.=dorsal valves of ovipositors. X 8

examined and that their presence may form a distinct sub-family character

The specimens examined are as follows -

- 1 *Anacridium aegyptium*, L
- 2 *Calliptamus italicus*, L
- 3 *Pezotettix giornai*, ( Rossi )
- 4 *Schistocerca paranensis*, Försk
- 5 *S gregaria* Försk
- 6 *Patanga suocincta* L
- 7 *Palaciosa khandelensis*, Bolivar
- 8 *Podisma* sp

#### THE ANATOMY OF THE VESICLES —

The vesicles in question are situated, one on each side of the gonopore, in the membranous area between the 8th sternite and the base of the ventral valves of the ovipositors. Normally they are hidden from view beneath the sub genital plate of the 8th sternite ( Figs. 1 and 2 ) Each vesicle has the form of a blind membranous

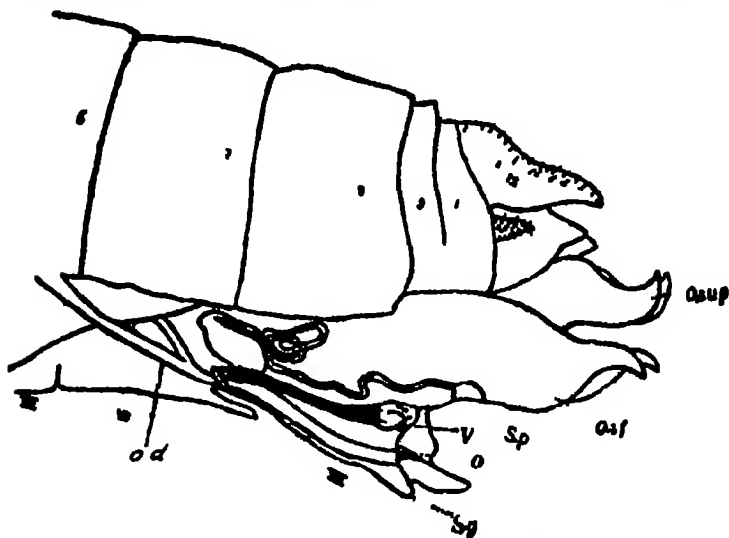


Fig 2. The same as the figure first seen from lateral aspect, the ventral valves of ovipositors partly dissected to show the opening of spermatheca o d = oviduct The rest as in the fig 1 X 8

pouch projecting into the body cavity on either side of the gonoduct and attached to muscle bands which are inserted into the apodeme of the 8th sternite ( Figs 2 and 3 )

The histology of the vesicles —

A longitudinal section of the wall of the vesicle, under study,

shows the following structures from without inwards :—

1. A thin noncellular layer of chitin.
2. A hypodermal layer and,
3. A very thin layer of the basal membrane.

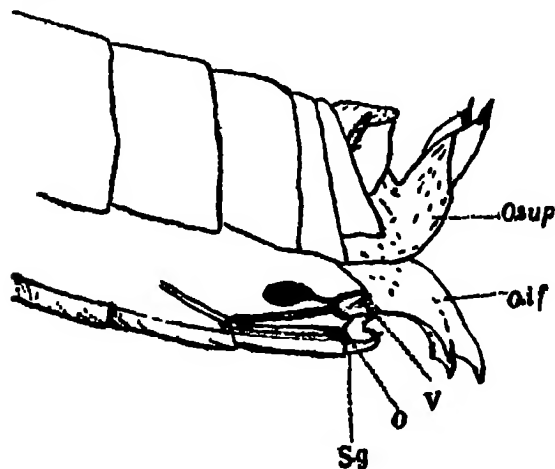


Fig. 3. The posterior extremity of abdomen of *Pezotettix giorna*.  
 Explanations as in the fig 1 X 10

The chitinous layer which is formed by the secretion of the hypodermis, is pierced through by a number of fine canalicules or ducteoles with chitinous lining ( Fig. 5 C ) The chitinous layer is not of uniform thickness ; towards the bottom of the pouch it is somewhat thinner than elsewhere ( Fig. 4 )

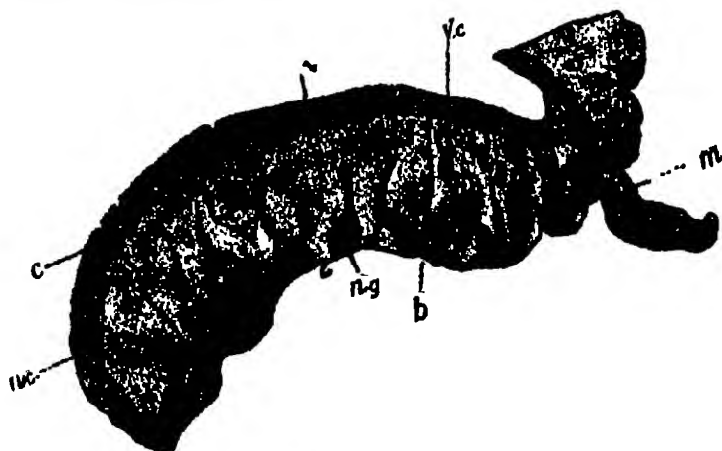


Fig 4. A portion of a longitudinal section of the oviductory vesicle, b.=basal membrane; c.=canalicule, l.=chitinous layers, m.=muscle band, n.c.=nucleus of a hypodermal cell, n. g.=nucleus of a glandular cell, s.=secretion, v. c.=collecting vesicle, X 375.

The hypodermis is composed of elongated cells each containing a large, irregular more or less spherical nucleus with a large number of chromatin granules (Fig 5 nc.) The cytoplasm of the hypodermal cells shows a reticular appearance after fixation. The basal membrane of these cells is extremely thin.

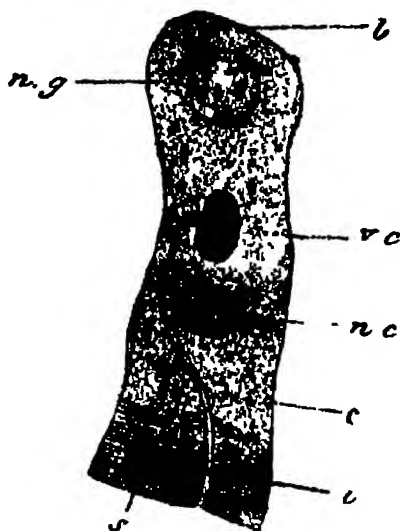


Fig 5. One of the hypodermal cells surmounted by a glandular cell.  
Explanations as in the Fig 4 X 1075

In between and at the base of the hypodermal cells are found certain typical glandular cells with a large nucleus containing chromatin granules. The cytoplasm of the glandular cells when fixed with common fixatives shows a fine granular structure. Each of these cells contains a form of a small vesicle (Fig 5 Vc.) which collects the secretory product of the cell and passes it on into the cavity of the pouch along the path of the canalicule (Fig. 5 c)

#### THE HOMOLGY OF THE VESICLES —

Similar type of vesicles—Coxal vesicles—are described by OUDEMANS (1888) in *Thysanura*. Larvae of *Agelastica alni* and *Melasoma populi* also possess similar vesicles, but in their case the turgidity of the organ is followed by ejection of blood (reflex bleeding).

The vesicles of the type described above are also found in Orthoptera in general. CUENOT (1896) finds a vesicle at the base of the elytra of *Ephippigarr bruneri*. VOSSELER (1903) describes a vesicle situated under the pronotum of *Oedaleus senegalensis* and a similar one near the articulation of coxae in *Eugaster guyoni*. HOLLANDE (1926) also describes certain vesicles of reflex bleeding in *Eugaster spinulosus*.

The vesicles of Acridinae are, however, associated with the genitalia of the female only. Morphologically they may be considered as homologous with the coxal glands of Thysanura. But then they are found only in Acridinae. Physiologically they may possibly be similar to the lateral sacculi found in the female *Bombyx mori*, where the secretion is ejected at the time of copulation. They are therefore considered as odoriferous organs which attract the male.

*Resumé* —

- (1) Glandular vesicles are present one on each side of the gonopore of Acridinae.
- (2) The vesicles are protrusible, the movement being controlled by a set of muscle bands attached at one end to the base of the pouch and at the other end to the apodeme of the 8th sternite.
- (3) Histological studies indicate the glandular nature of these vesicles.

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# STUDIES IN INDIAN PUFFERS OR GLOBE FISHES

## II. THE BLOOD VASCULAR SYSTEM OF TETRODON OBLONGUS (Bloch).

By

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The vascular system (Figs. 1, 2, 3, 4, 5, 6 & 7) of *Tetrodon oblongus* consists of the heart, arteries, veins and capillaries, through which the blood is propelled forward in a definite direction by the

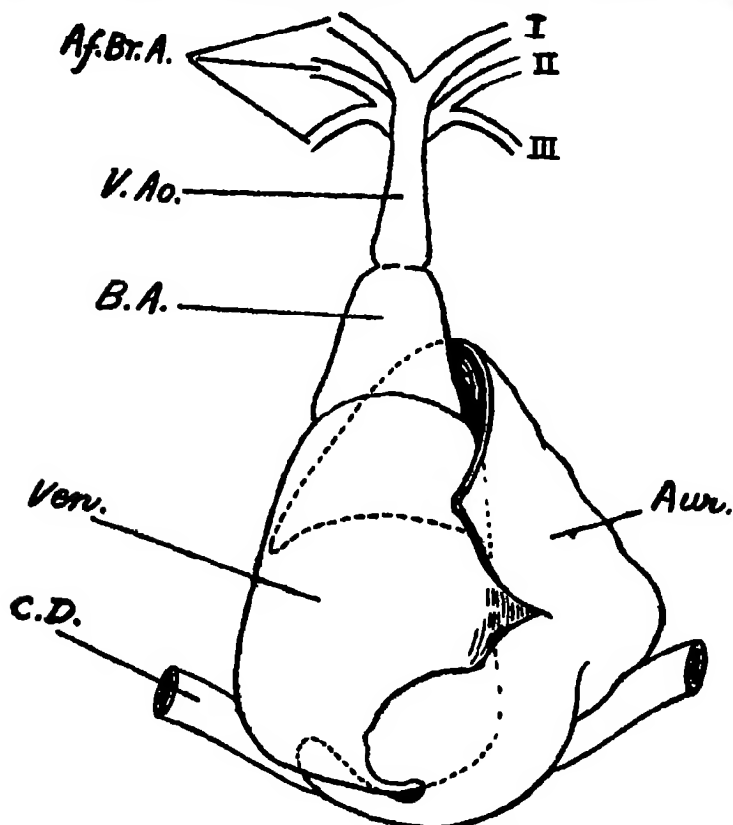
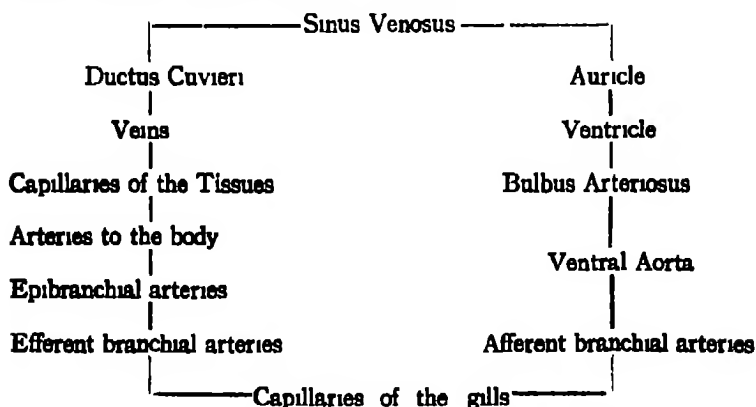


Fig. 1 —Ventral View of the Heart of *T. oblongus*.

Af Br A —Afferent Branchial Artery, Aur.—Auricle, B. A.—Bulbus Arteriosus. C. D —Cuvierian Duct V. Ao.—Ventral-Aorta Ven.—Ventricle. I, II, & III —Afferent Branchial Arteries.

rhythmical contractions of the heart. The course of the blood may diagrammatically be represented as follows —



The circulation of blood can be described under different following heads :—

1 *Heart* —The heart (Figs. 1 & 2) in *Tetrodon oblongus* consists of the sinus venosus, the auricle and the ventricle and is surrounded by the thin pericardium. The heart nearly fills the pericardial cavity which is closed off from the abdominal coelom by a fibrous transverse septum.

*Sinus venosus* —The sinus venosus (Fig. 4 Sin. V.) is a thin walled transversely elongated chamber placed at the base of the pericardial cavity. The large veins opening into it are the paired cuvierian ducts (into which open vessels from the anterior as well as posterior regions of the body), the paired subclavian and lateral veins, and the unpaired hepatic and inferior jugular veins. The sinus venosus together with the cuvierian ducts forms a horse-shoe shaped structure with the ends pointing dorsalward. It encircles the oesophagus ventrally and laterally.

The sinus venosus communicates anteriorly with the auricle through the sinu-auricular aperture (Fig. 2 Si. Au. Ap.), situated in the middle of its ventral wall. This opening is guarded by a valve (Fig. 2 Si. Au. V.), consisting of two membranous flaps (lips) anterior and posterior in position. This valve prevents the backward flow of blood from the auricle into the sinus venosus during the contraction of the former.

*Auricle*.—The auricle (Aur.) is a very irregularly shaped structure. It lies on the left side of the ventricle and extends slightly on its anterior and posterior sides and encircles it on both the ventral and dorsal sides. The wall of the auricle is thicker than that of the sinus venosus and is strengthened internally, especially on its dorsal and ventral portions by interlacing muscle bands, the *musculi pectinati*;



(Fig. 3 M. P.). It is separated from the ventricle by short horizontal auriculo-ventricular constriction. In the latter is situated the auriculo-ventricular orifice (Fig. 2 Au. Ve. Ap.) through which the auricle opens into the ventricle. It is guarded by a pair of vertical semilunar pocket-shaped valves, one anterior and the other posterior (Fig. 2 Au. Ve. V.). They are membranous flaps which project into

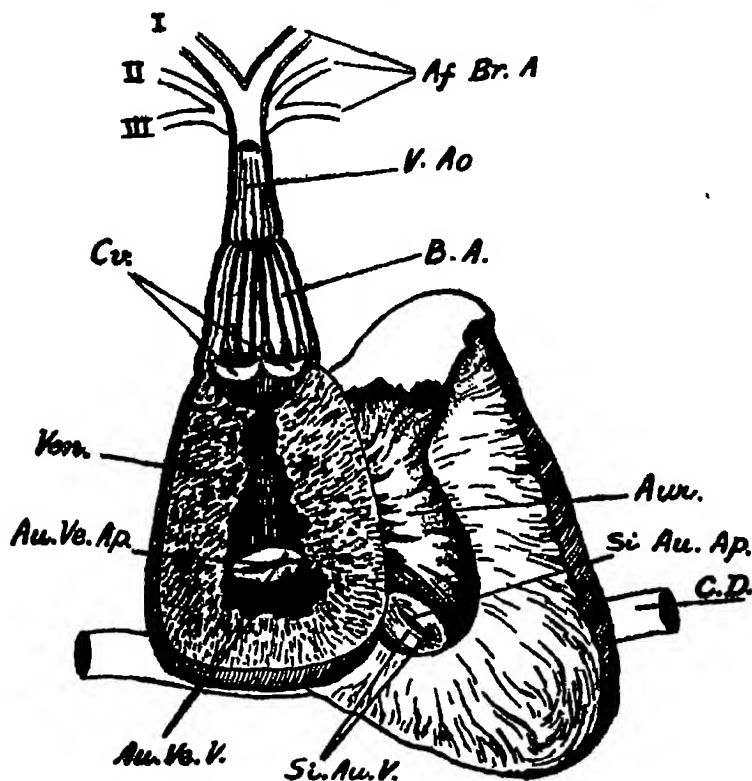


Fig. 2—The Heart of *T. oblongus* dissected from the ventral surface.

Au. Ve. Ap.—Auriculo-Ventricular Aperture, Au. Ve. V.—Semilunar Pocket-shaped valves, Cv—Semilunar Valves, Si. Au. Ap.—Sinauricular Aperture, Si. Au. V.—Sinu-auricular Valve. Remaining letters same as in Fig. 1

the cavity of the ventricle, with the cavities of the pockets facing the ventricle. The mechanism of this kind of valves consists of the pockets being swollen out by the blood flowing into them and thereby closing the orifice.

**Ventricle.**—The ventricle (Ven.) is antero-posteriorly elongated cylindrical structure, situated somewhat ventral to the auricle. Its posterior portion as already mentioned, is partly enclosed by the auricle. The walls of the ventricle are very thick and muscular and

are produced internally into ridges—the *columnae carnae* (Fig. 3 Col. C.). The latter reduce its lumen to a considerable extent and give the ventricle a spongy texture. The structure that follows the ventricle is the *Bulbus Arteriosus* which is nothing but a greatly dilated basal end of the ventral aorta. Between the ventricle and the bulbus arteriosus there is a deep constriction or furrow which appears to indicate the remains of the conus, since in this region there is a pair of semilunar valves (Fig. 2 Cv.) located one above the other dorsoventrally. They guard the opening of the ventricle into the bulbus. They are pocket-shaped and have semilunar edges. Their cavities point towards the bulbus arteriosus.

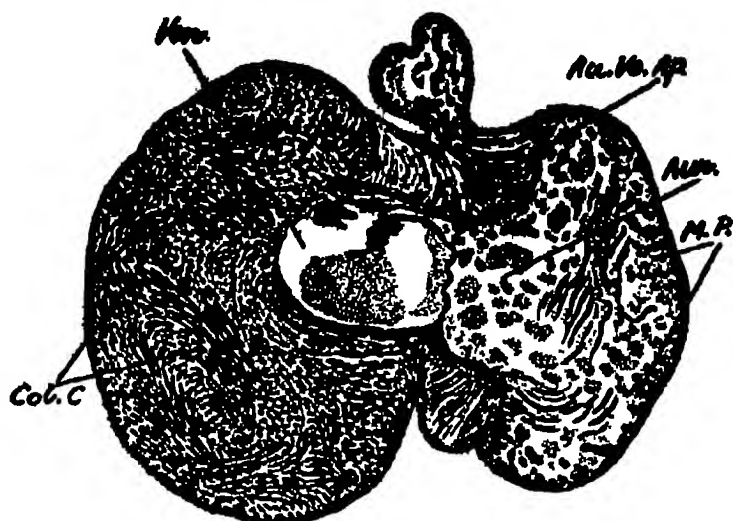


Fig. 3 —Transverse Section of the Heart of *T. oblongus* passing through the Auricle and Ventricle.

Col. C —Columnae Carnae , M. P —Musculi Pectinati. Remaining letters same as in Figs. 1 & 2.

**Bulbus arteriosus:**—The structure of the heart of a higher Teleost deviates generally from that of a lower Teleost and other fishes like the Elasmobranchs as far as the region of the conus is concerned. The lower Teleostomes (such as the Chondrostei, Polypterini and Lepidosteoides) possess a well developed muscular and contractile conus which is a continuation of the distal end of the ventricle. In the higher Teleostomes (such as the Teleostei) on the other hand, the conus is reduced and is replaced wholly or partially by a non-contractile and non-muscular structure called "The bulbus Arteriosus" (B. A.). Thus the bulbus arteriosus does not constitute any part of the heart but it is simply a swollen proximal or basal part of the ventral aorta. The latter is greatly swollen at its origin from

the ventricle and its internal surface is produced into longitudinal folds. Its walls as well as the folds are composed of the fibrous connective tissue without muscle strands.

*Ventral Aorta* —The bulbus arteriosus is followed by the distal part of the ventral aorta (V. Ao.) which runs along the ventral surface of the pharynx and between the ventral extremities of the gill arches. It is a non-contractile and tubular structure and its walls are composed of fibrous connective tissue. It gives rise to three afferent branchial arteries (Af. Br. A.) on each side.

*The Afferent Branchial Arteries* —The first pair of the afferent branchial arteries is formed by the bifurcation of the ventral aorta itself and supplies blood to the first pair of gills. Each of them runs along the outer grooved surface of the first branchial arch, supplying blood through numerous branches along its whole length to the anterior and posterior gill lamellæ of the first holobranch. The second and third afferent branchial arteries of each side seem to arise from the common vessel arising from the ventral aorta at a little distance behind the first. This common vessel is divided internally by a fine septum into two branches almost at its origin but externally it appears to be continued as one for an appreciable distance where the two afferent arteries diverge from each other. The second and third afferent arteries of each side run almost parallel with the first of that side along the grooved surfaces of the second and third branchial arches respectively.

The function of the heart is to pump the blood to the gills. This pumping of the blood is effected by the rhythmical and successive contractions of the heart. These contractions are effected by muscle strands of the muscular tissue of which the heart is made. The contraction of the different parts of the heart takes place in a regular order; first the sinus, then the auricle and ventricle and finally it ends in the bulbus or ventral aorta. When the sinus venosus contracts, the blood, brought to it by the veins coming from different parts of the body, is forced forward into the auricle through the sinu-auricular aperture. But the blood is prevented from running backward into the ductus cuvier since the latter, being always full, is under a higher pressure than what is obtained in the auricle. The two membranous flaps which form the sinu-auricular valve, prevent the backward flow of the blood from the auricle into the sinus when the former contracts in its turn and drives the blood into the ventricle. The two semilunar pocket-shaped valves in the ventricle act likewise and prevent blood from flowing back into the auricle when the ventricle contracts. During the contraction of the ventricle, the blood passes into the bulbus arteriosus and thence into the ventral aorta. There is a pair of semilunar valves at the opening of the ventricle into the

bulbus arteriosus and any return of the blood into the ventricle is made impossible by the presence of these valves. The blood then passes into the three pairs of afferent branchial arteries in order of their origin and is taken ultimately into a great number of lamellar capillaries of the gills where the oxygenation of the blood takes place

*The Efferent Branchial Arteries* —The aerated blood from the several gill lamellæ is collected by a set of efferent capillaries into three pairs of blood vessels called "the efferent branchial arteries" (Fig. 4 Ef Br A.) corresponding to the three afferent branchials. There are only three such arteries on each side (since the fourth efferent branchial artery has disappeared along with the disappearance of the fourth gill). It should be noted here that the blood from the two demibranchs of each branchial arch i.e, from a single holobranch is conveyed to the lateral dorsal aorta of each side by single efferent vessel unlike that of the Dogfish in which a loop is formed in the gill region. Each efferent branchial artery is continued dorsally towards the lateral dorsal aorta (L. Ao.) of its side as the epibranchial artery (E. Br. A.). The three epibranchials of each side form the lateral dorsal aorta of that side. The paired lateral aortae thus formed unite posteriorly on the dorsal side of the oesophagus and form the dorsal aorta (D. A.). Anteriorly they run towards the base of skull as the common carotid arteries which will be described in connection with the head arteries.

*The Arteries of the Head* (Fig. 4) —The common carotid artery (C Car. A.) which is the anterior continuation of the lateral aorta divides into the external and internal carotids

The external carotid (Ex. Car) is termed as "Orbitonasal" by Allen, Nils Rosen and other authors. It runs forward along the ventral surface of the skull and extends right up to the anterior end of the head. On its way it gives off several branches supplying the eyes, eye-muscles, nostrils etc. While the internal carotid (I. Car.) after running for a short distance enters the parasphenoid and meets its fellow from the other side and thus forms the "Circulus Cephalicus", the characteristic structure of the Teleosts (Cir. C.).

A pair of arteries is given off both anteriorly and posteriorly from the circulus cephalicus at the place of the union of the two internal carotids. The anterior pair forms the Optic arteries (Opt. A.) and the posterior, the Cerebral arteries (Cer. A.). The Optic arteries have a very short common root since they soon diverge out from each other. Each of them, then, passes out towards the eye of its side along the corresponding optic nerve and enters the retina along with the nerve. While the Cerebral arteries arise like the optic arteries but on the opposite side from the circulus cephalicus. They enter the cranial cavity through the parasphenoid and then they separate out immediately after their entrance into the right and left cerebral

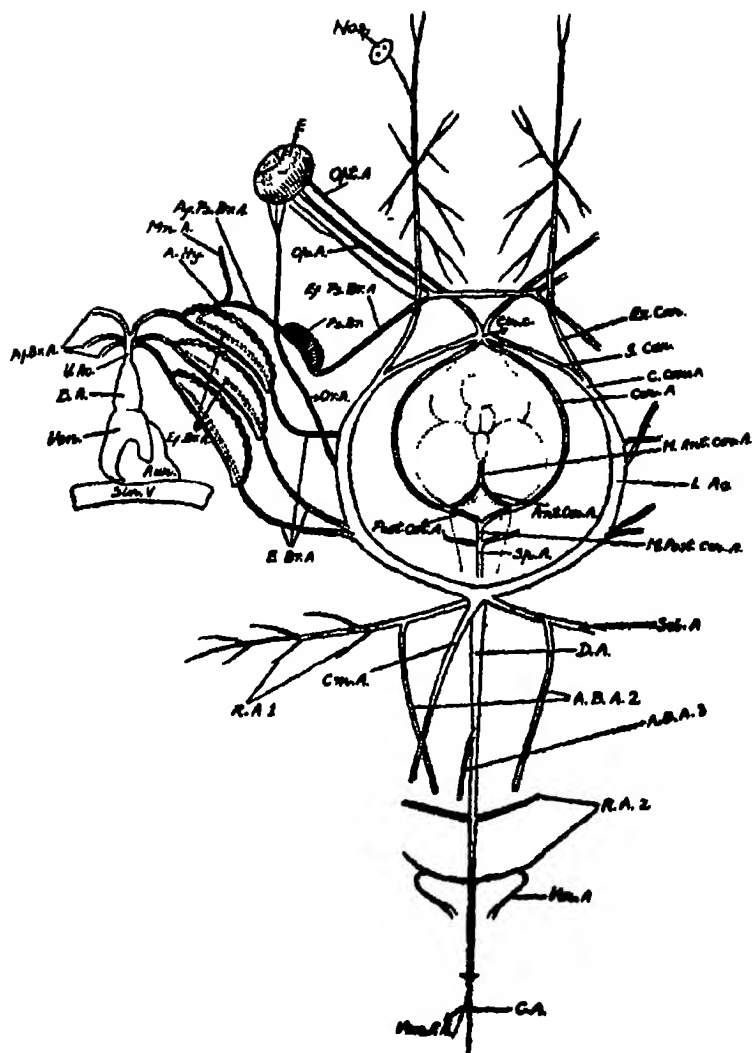


Fig. 4 — Arterial System of *T. oblongus*.

A. B. A. 2—Artery to the Air Bladder from the Subclavian artery, A. B. A. 3—Artery to the Air Bladder from the Dorsal Aorta, A. Hy.—Hyoidean Artery, Af Br. A—Afferent Branchial Artery, Af Pa. Br. A—Afferent Pseudo-branchial Artery, Ant Cer. A—Anterior Cerebral Artery, Aur—Auricle, B. A—Bulbus Arteriosus, C. A—Caudal Artery, C. Car. A—Common Carotid Artery, Cer. A—Cerebral Artery, Cir. C.—Circulus Cephalicus, Cm. A—Coeliaco Mesenteric Artery, D. A.—Dorsal Aorta, E.—Eye; E. Br. A—Epibranchial Artery, Ef Br. A—Efferent Branchial Artery, Ef Pa. Br. A—Efferent Pseudo-branchial Artery, Ex. Car.—External Carotid Artery, I. Car.—Internal Carotid Artery, L. Ao.—Lateral Dorsal Aorta; M. Ant. Cer. A—Median Anterior Cerebral Artery, M. Post. Cer. A—Median Posterior Cerebral Artery, Mn. A—Mandibular Artery, No. 1—Nostril, Op. A.—Ophthalmic Artery, Opt. A.—Optic Artery, Or. A.—Orbital Artery, Post. Cer. A—Posterior Cerebral Artery, Ps. Br.—Pseudobranch; R. A. 1—Arteries to the Kidney from the Subclavian Artery, R. A. 2—Arteries to the Kidney directly from the Dorsal Aorta, Sci. A.—Subclavian Artery; Sin. V.—Sinus Venosus, Sp. A.—Spinalis Artery, V. Ao.—Ventral Aorta, Ven.—Ventricle, Ven. F. A.—Artery to the Ventral Fin, Ver. A.—Vertebral Artery

arteries. Each of them curves out by the side of the pituitary body and forms a sort of a semicircular loop within the cranial cavity. Posteriorly the two loops approach each other in a mid-ventral line between the optic lobes, where each of them again divides into two branches forming the anterior and posterior cerebral arteries (Ant Cer A, Post Cer A). The anterior cerebrals after a short course unite with each other beneath the optic lobes and form the combined median anterior cerebral artery (M. Ant. Cer. A). The latter runs forward along the ventral portion of the brain anterior to the cerebellum and thereby supplies blood to this part of the brain. The posterior cerebrals likewise meet each other and form the combined median posterior cerebral artery (M. Post. Cer. A.), which proceeds towards the posterior region along the ventral surface of the brain. The combined median posterior cerebral artery gives out a small pair, one on either side beneath the medulla oblongata. It supplies blood to the fifth, seventh, eighth and ninth cranial nerves and also to the auditory organ. The median artery is then continued behind as the spinalis or basilaris (Sp. A) artery which runs along the ventral surface of the spinal cord throughout its length.

The Orbital artery (Or. A) arises on each side of the lateral aorta a little behind the opening of the first epibranchial artery into the same. It is known as orbital artery (Goodrich) or external carotid (Nils Rosen). It runs forward towards the orbit dorsal to the pseudobranch and supplies blood to the region surrounding the eye.

The Pseudobranchial or Hyoidean artery (A. Hy.) is a fairly large vessel arising on each side from the ventral end of the first efferent branchial. It is called the "Hyoidean or Pseudobranchial artery" which on leaving the branchial arch gives rise to a small branch called Mandibular artery (Mn A). The latter supplies blood to the mandibular and to the opercular regions. The main hyoidean trunk then turns round dorsally and runs along the internal surface of the operculum as the "Afferent Pseudobranchial artery" (Af. Ps. Br. A.). After reaching the pseudobranch it breaks up into several capillaries in the filaments of that structure. The blood from the pseudobranch is again collected by the efferent pseudobranchial capillaries. All these unite to form the "Efferent Pseudobranchial artery" (Ef. Ps. Br. A) which after crossing over the external carotid divides into two branches. One of them is known the Ophthalmic artery (Op. A.) and the other running inward, meets its fellow from the other side above the parasphenoid. The ophthalmic of each side proceeds towards the eye along the optic nerve of its side and parallel with the optic artery already described. It finally perforates the sclerotic coat and supplies blood to the choroid gland of the eye.

Thus it will be seen from the above description that the pseudobranch is supplied with arterial blood unlike the other gills. It, therefore, appears that it has lost its original respiratory function though its morphological structure is almost similar to that of a demibranch of an ordinary gill. The function of the pseudobranch is not yet ascertained. Joh. Muller (6) suggested that the pseudobranch is a gland furnishing an internal secretion, and that the object of the included capillary system of the pseudobranch is to equalise the intraoptical pressure by smoothing down the pulsation of the heart. According to Cole and Johnstone (6) there is no evidence of the elaboration of any internal secretion and the blood in the ophthalmic artery has already passed through the branchial capillaries before reaching the pseudobranch.

*The Hypobranchial Arteries* (Fig. 5) —They consist of small vessels, arising from the ventral ends of the three pairs of efferent branchial arteries. The prominent of them is a small commissural vessel (Com. A. 2.), arising from the ventral end of the second efferent branchial artery. It unites with its fellow of the other side below the ventral aorta and the combined vessel thus formed is called the "Median Hypobranchial Artery" (Md. Hy. Br. A.). The latter runs down for some distance in a vertical direction through the sternohyoid muscles and then turns behind towards the posterior side. It gives off a single "Sternohyoid" artery (St. A.) to the sternohyoid muscles while passing through them. Then the median hypobranchial artery is continued towards the posterior end and it gives off a pair of lateral branches at the anterior end of the pericardial cavity. Each of the laterals may be called as the "Pericardial" artery (Peri. A.) which runs on each side along the outer margin of the pericardial cavity and finally disappears in the muscles of the pectoral girdle. On its way it gives off several smaller branches, supplying blood to the heart, the pericardium, the air-sac and to the pectoral muscles. Behind the pericardials, the median hypobranchial artery becomes small and supplies blood to the ventral longitudinal muscles of the air-sac and to the air-sac itself (A. S. A.). Each commissural from the second efferent branchial artery gives off in addition a small branch towards the anterior side before joining its fellow from the other side. This small Buccal Artery (Bu. A.) runs forward and supplies blood to the muscles on the ventral wall of the buccal cavity.

Similarly there arises on each side a commissural vessel from the ventral ends of the first and third efferent branchial arteries. The commissural from the first (Com. A. 1) is small and divides into two branches at some distance from its origin. The anterior of the two runs in front and the posterior one joins the commissural from

the second efferent branchial artery. The commissural from the third (Com. A. 3) likewise divides into two branches. The anterior of them runs forward and opens into the commissural from the second.

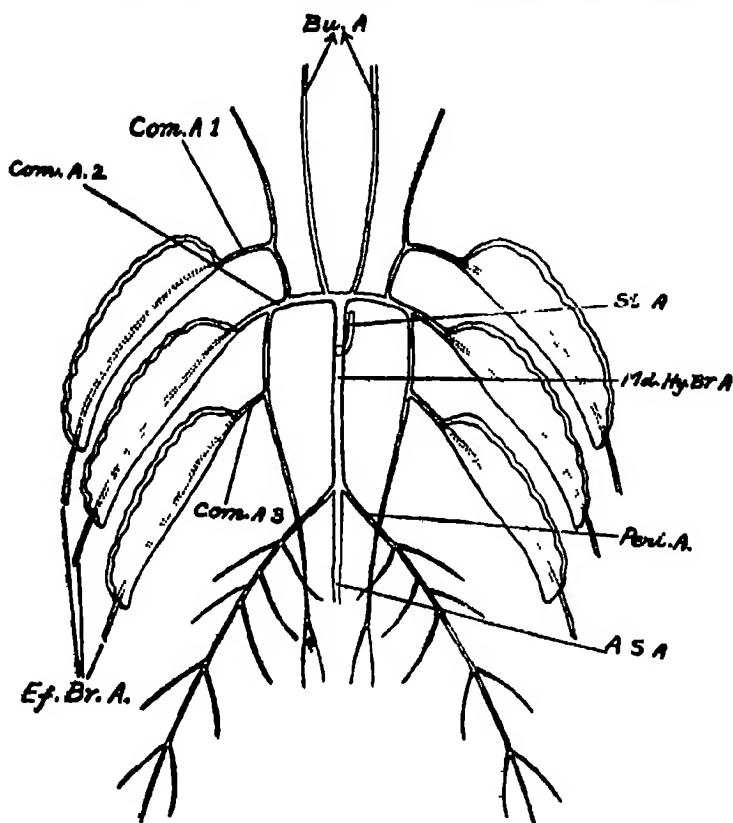


Fig 5 —The Hypobranchial Arteries of *T. oblongus*.

A. S. A.—Artery to the Air Sac, Bu. A.—Buccal Artery, Com. A. 1—Com. A. 2. and Com. A. 3—Commissural Vessels from the First, Second & Third Efferent Branchial Arteries respectively, Ef. Br. A.—Efferent Branchial Artery, Md. Hy. Br. A.—Median Hypobranchial Artery, Peri. A.—Pericardial Artery, St. A.—Sternohyal Artery.

The posterior branch of the same runs behind and breaks into smaller vessels below the oesophagus. It supplies blood to the dorsal region of the heart, and to the pharyngeal and oesophageal regions

**The Dorsal Aorta and its Branches** —The dorsal aorta (Fig. 4) gives out several branches which are described below.

(1) **The Subclavian Arteries** —A pair of large vessels arises from the dorsal aorta at its very beginning. They are called the "Subclavian arteries" (Scl. A) supplying the paired pectoral fins. Immediately after their origin they proceed out towards the body-wall



and on their way they give off a stout branch to the air bladder (A. B. A. 2). While running outward towards the fins they pass through the lobes of the kidneys (R. A. 1) to which they supply blood by several smaller branches. Finally each of them enters the pectoral girdle and supplies the pectoral fin of its side.

(2) *The Coeliaco-mesenteric Artery*.—The coeliaco-mesenteric artery (Figs 4 & 6 Cm. A.) is an unpaired vessel lying to the right side of the body. It originates ventrally from the point of the union of the two lateral aortae to form the dorsal aorta. Immediately after its origin the coeliaco-mesenteric proceeds posteriorly between the oesophagus on one side and the liver on the other. It first gives a stout branch called the Hepatic artery (Fig. 6 Hep. A.). The latter divides into smaller branches, all of which enter the liver at different points. The main trunk then runs along the stomach and gives rise

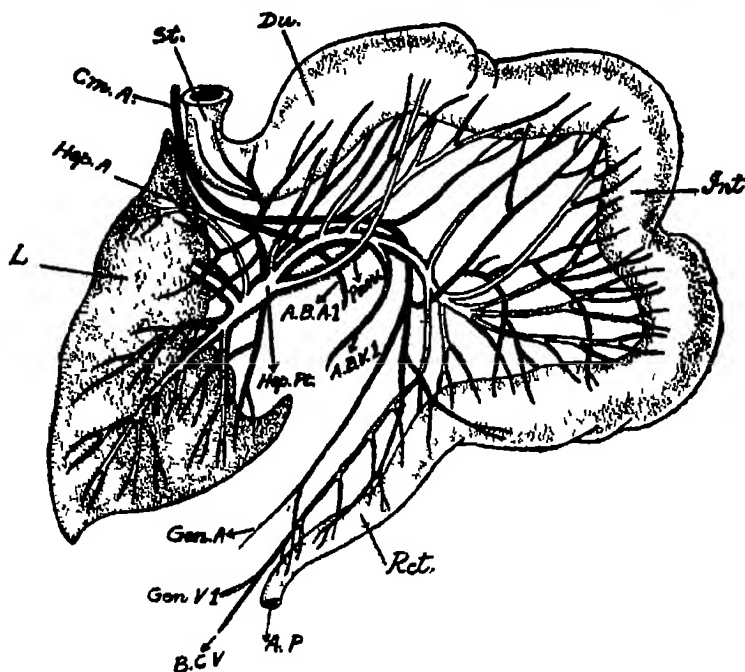


Fig. 6 —*Vascular Supply of the Alimentary Canal.*

(The black lines show the Arteries and the others show the Veins.)

A. B. A. 1—Artery to the Air Bladder from the Coeliaco-mesenteric Artery, A. B. V. 1—Vein from the Air Bladder joining the Hepatic Portal Vein, A. P.—Anal Aperture, B. C. V.—Branch from the Caudal Vein joining the Hepatic Portal Vein, Cm. A.—Coeliaco Mesenteric Artery; Du.—Duodenum, Gen. A.—Genital Artery, Gen. V 1—Genital Vein joining the Hepatic Portal Vein, Hep. A.—Hepatic Artery; Hep. Pt.—Hepatic Portal Vein, Int.—Intestine, L.—Liver, Pan.—Pancreas, Rct.—Rectum, St.—Stomach.

to several vessels supplying the oesophagus, stomach, spleen and air-bladder (Fig. 6 A B. A 1) Onward the original vessel breaks up into some more branches supplying the intestine, rectum, and mesentery. Lastly the terminal part of the Coeliaco-mesenteric artery gives off branches supplying the anus, gonads and urinary bladder (Fig 6).

(3) *The Air-bladder Artery* —Behind the coeliaco-mesenteric and the sub-clavian arteries, the dorsal aorta gives off another unpaired artery supplying blood to the air-bladder (A. B A. 3).

(4) *The Renal Arteries* —The dorsal aorta gives off two pairs of the renal arteries (R. A. 2) at short intervals, behind the air-bladder artery. They supply blood to the posterior lobes of the kidneys. The second pair of the renal arteries breaks up into a smaller branch which supplies blood to the vertebral column (Ver. A.).

(5) *The caudal Artery*.—The dorsal aorta lies beneath the vertebral column for some distance and then at a short distance behind the origin of the second renal artery it lies within the groove formed by the succeeding trunk vertebrae. Posteriorly that is behind the anus it enters the hæmal canal of the caudal vertebrae and then the dorsal aorta is known as "The Caudal artery" (C. A.). The latter gives off at its beginning an unpaired vessel to the ventral fin (Ven. F. A.).

(6) *The Segmental Arteries* —They consist of several paired vessels which arise from the dorsal aorta on its way towards the posterior side. They supply blood to the body-wall and to the trunk and tail muscles.

## THE VEINS.

The impure or deoxygenated blood from all parts of the body is collected and carried back to the heart by thin-walled vessels called "The Veins" (Figs. 6 & 7) The veins coming from the different parts of the body may be described as follows.—

### I. Veins from the anterior region in front of the heart.

- (a) The Anterior Cardinals
- (b) The unpaired Inferior Jugular.
- (c) The Clavicular veins.

### II Veins from the posterior region behind the heart.

- (A) Veins in the abdominal cavity.
  - (a) The Posterior Cardinals.
  - (b) The Renal Portal system.
  - (c) The Hepatic Portal system.
  - (d) The Genitals.
  - (e) The Air-bladder vein,

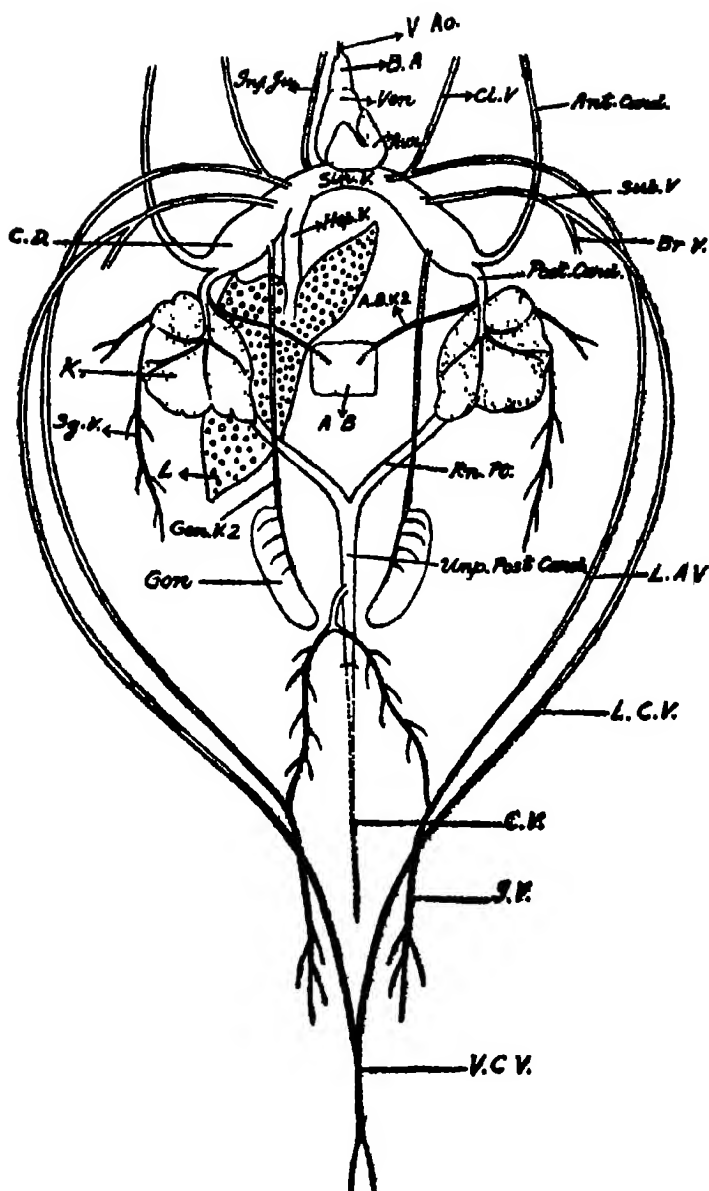


Fig. 7 —Venous System of *T. oblongus*.

A. B.—Air Bladder; A. B. V. 2—Vein from the Air Bladder opening into the Posterior Cardinal Vein, Ant. Card.=Anterior Cardinal Vein, Aur=Auricle; B. A.=Bulbus Arteriosus, Br. V.=Brachial Vein; C. D.=Cuvierian Duct; C. V.=Caudal Vein, Cl. V.=Clavicular Vein; Gen. V. 2=Genital Vein opening into the Cuvierian Duct, Gon.=Gonad, Hep. V.=Hepatic Vein; I. V.=Iliac Vein, Inf. Ju.=Inferior Jugular Vein, K.=Kidney, L.=Liver; L. A. V.=Lateral Abdominal Vein, L. C. V.=Lateral Cutaneous Vein; Post. Card.=Posterior Cardinal Vein, Rn. Pt.=Renal Portal Vein; Sg. V.=Segmental Vein, Sin. V.=Sinus Venosus, Sub. V.=Subclavian Vein; Unp. Post. Card.=Unpaired Posterior Cardinal Vein, V. C. V.=Ventral Caudal Vein; Ven.=Ventricle,

## (B) Veins in the body-wall.

(a) The Lateral Abdominals.

(b) The Lateral Cutaneous

I. All the blood from the head region is returned to the heart by the large paired anterior cardinals, unpaired inferior jugular and by the paired clavicular veins coming from the clavicular muscles

(a) *The Anterior Cardinals*.—The paired anterior cardinals (Fig. 7 Ant. Card.) are large thin-walled vessels which drain the blood from the head, eyes, brain, branchial regions etc. They start from the anterior portion of the head and are joined on their way by smaller vessels from the orbito-nasal and branchial regions. They, then, run towards the heart along the ventral surface of the skull and dorsal to the branchial arches. The anterior and posterior cardinals of each side open side by side into the wide transverse vessel, the "Cuvierian duct" (C. D.). The latter is continued into the sinus venosus.

(b) *The Inferior-Jugular*.—The unpaired inferior jugular vein (Inf. Ju.) originates from the ventral margin of the branchial arches and runs above the ventral aorta for a short distance. It then bends outside and proceeds towards the sinus venosus by the side of the heart. It opens into the right side of the sinus venosus.

(c) *The Clavicular Veins*.—They consist of two slender vessels (Cl. V.) arising from the antero-lateral side of the skull and from the clavicular muscles. They proceed towards the sinus venosus along the ventral region of the gills. Each of them collects blood from the clavicular muscles and finally joins the lateral abdominal vein (to be described subsequently) of its side.

II. The Veins that drain off the blood from the region behind the heart can be described under two heads as mentioned in the table given above.

(A) The veins coming from the abdominal cavity consist of five principal vessels as described below.

(a) *The Posterior Cardinals*.—The Posterior Cardinal veins (Post. Card.) consist of two wide but very short vessels owing to the shifting of the kidneys towards the anterior end of the abdominal cavity. Each of them commences in the compact kidney of its side and then approaches the anterior cardinal of the same side in the region of the heart. However it opens separately into the Cuvierian duct as mentioned above. In addition to the blood from the kidney, the posterior cardinal receives venous blood from the air bladder (A. B. V. 2). A small vein starts on each side from the dorsal wall of the air bladder and after running outward towards the region of the kidney, it empties its contents into the lumen of the posterior cardinal vein.

(b) *The Renal Portal System* :—The caudal vein (C V.) from the tail runs towards the anterior side through the haemal canal, immediately beneath the caudal artery. It, then, emerges into the abdominal cavity and runs as a single vessel for a short distance. This undivided portion of the caudal vein may be called as the "Unpaired Posterior Cardinal" (Unp. Post. Card.) vein. It is joined on its way by a single vein, formed by the union of two vessels one from each side. The latter are the inner branches of the iliac vein (I. V.). It then divides into the right and left renal portal veins (Rn. Pt.) at some distance behind the air bladder. Each of the branches curves out and proceeds towards the kidney of its side and enters the posterior lobe of the same. It breaks into several smaller branches in that organ. The kidney also receives an additional supply of venous blood from the muscles of the trunk through several segmental veins (Sg. V.). Finally the blood from the kidney is drained off by the posterior cardinal and thence to the cuvierian duct.

(c) *The Hepatic Portal System* (Fig. 6) —The blood from the different parts of the alimentary canal, also a small portion from the gonads (Gen. V. 1), the urinary bladder and the two ureters, together with a small portion of blood from caudal vein (B. C. V) and the blood from the ventral region of the air bladder (A. B. V. 1), is collected by a series of smaller veins constituting the Hepatic Portal system. These several veins join each other as they run towards the liver and thereby give rise to a principal vein called "The Hepatic Portal Vein" (Hep. Pt.). The latter runs towards the liver and finally discharges its contents into it. It should however be noted that the hepatic portal vein does not enter into the liver by a single trunk but it divides again into a small number of branches before entering into the liver. They, then, enter the liver independently and break into numerous capillaries in the interior of that organ.

The blood from the liver is recollected by a number of small veins which ultimately unite into a short, wide and unpaired vein called the "Hepatic Vein" (Fig. 7 Hep. V). The latter opens directly into the sinus venosus.

(d) *The Genitals* .—A stout vein (Fig. 7 Gen. V. 2) starts from each gonad (either testis or ovary) and runs forward towards the heart along the ventral surface of the air-bladder. It finally opens directly into the cuvierian duct of its side. It should be mentioned here that in a few specimens it was found that the two genital veins joined each other and then the single vessel, thus formed, opened into the right cuvierian duct.

(e) *The Air-bladder Vein* —A small vein (Fig. 7 A. B. V. 2) starts on each side from the dorsal wall of the air bladder and after running outward towards the region of the kidney, it empties its con-

tents into the lumen of the posterior cardinal vein of its side. It may be noted here that a portion of the venous blood from the ventral region of the air bladder is collected by a single slender vessel. The latter opens (as described above) into the hepatic portal vein on its way towards the liver (Fig 6 A. B. V. 1.)

(B) The Veins running along the body wall consist of two paired loop like vessels as described below:—

(a) *The Lateral Abdominals* —These paired veins arise from the post-cloacal myotomes, on the ventral region of the tail by the side of the ventral fin. Each of them is formed by the union of several smaller vessels coming from the muscles of the surrounding area of the ventral fin and some from the ventral fin itself. They, thus, give rise to a single vessel on each side of the ventral fin. It seems to correspond to the Ilac vein (I V.) of the Dogfish. Each of them proceeds forward and divides into two branches as soon as it enters the abdominal cavity. The inner of the two receives several segmental veins from the precaudal myotomes and from the cloacal region. It, then, joins its fellow of the opposite side and the common vessel thus formed opens into the unpaired posterior cardinal vein as described above. The outer branch on the other hand continues forward as the well-known "Lateral Abdominal Vein", on each side (Fig 7. L. A. V.) It runs forward along the latero-ventral side of the body, immediately external to the peritoneum and is more or less embedded in the ventral longitudinal muscles. On its way towards the heart it receives several branches from the trunk muscles. It turns dorsalwards in the pectoral region and then receives a branch from the clavicular muscles as described above. The common vessel thus formed turns again towards the posterior side and soon enters the sinus venosus.

(b) *The Lateral Cutaneous* —In the mid-ventral region of the tail behind the ventral fin, a vein is formed by the union of two smaller vessels. The single vein so formed may be called for convenience sake "The Ventral Caudal Vein" (V. C. V.) as distinguished from the other caudal vein already described. It runs along the mid-ventral line as far as the ventral fin, where it divides into two branches one running on each side of the fin. It, then, proceeds along the lateral bodywall as the "Lateral Cutaneous Vein" (L. C. V.) below the skin and running almost parallel with the lateral abdominal vein mentioned above. On each side it runs as far as the pectoral region where it joins anteriorly with the Brachial vein (Br. V.) of its side. The common vein thus formed, carrying blood both from the pectoral girdle and from the lateral cutaneous vein may now be called the "Sub-Clavian Vein" (Sub. V.). The latter enters finally into the sinus venosus.

Thus it will be seen that certain portion of the venous blood from caudal region reaches the heart directly without the intervention of

either the renal portal or hepatic portal systems, whereas the remaining main portion of blood has to pass through one of the two portal systems

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TWO NEW SPECIES OF THE GENUS *DIPLOTRIAENA*  
(NEMATODA) PARASITIC IN THE  
COMMON INDIAN MYNA  
(*Acridotheres Tristis Tristis*).

By

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The parasitic worms described in this paper were collected from the body-cavity of the Myna on two occasions. A study of the structure of these worms revealed the presence of two distinct species in the lot.

*DIPLOTRIAENA ACRIDOTHEREI* N. SP.

The worms belonging to this species are long and white in colour. The males measure 35 mm.-52 mm. in length and have a maximum width of 0.487 mm. Females are much longer than the males and are 118 mm.-125 mm. long with a maximum breadth of 0.7 mm.-1.2 mm. The cuticle of the body appears to be unstriated in both the sexes. The worms taper towards the extremities, the anterior end being somewhat narrower than the posterior one. The trident measures 0.127 mm.-0.154 mm. in the male and 0.154 mm.-0.245 mm. in the female. Its anterior end is blunt. The oesophagus can be seen through the body-wall, in all the specimens, with the naked eye. It is divided into two parts—a short anterior and a very long posterior one. The posterior portion of the oesophagus, in all the specimens, appears black under the microscope. The length of the entire oesophagus is 8.61 mm.-8.691 mm. in the male and 9.17 mm.-11.072 mm. in the female. The short anterior part of the oesophagus is 0.21 mm.-0.227 mm. long in the male and 0.21 mm.-0.272 mm. in the female. The nerve ring is situated at 0.209 mm.-0.227 mm. from the anterior end in the male and 0.2 mm.-0.209 mm. from the same end in the female. The tail of the male measures about 0.1 mm. in length and is truncated. It is somewhat compressed dorsoventrally and expanded to some extent laterally in the cloacal region. The tail of the female is round and measures 0.290 mm.-0.372 mm. in length.

There are eleven pairs of caudal papillae in the male. Two pairs are preanal and the remaining ones postanal. The left papilla of the second preanal pair is, in some specimens, displaced and is situated by



the side of the anal aperture. Of the eleven pairs, five are situated on the margin of the tail. The spicules are unequal and dissimilar. The right spicule which measures 0.55 mm.-0.61 mm. is spirally coiled and is the smaller of the two. The left spicule is straight, much longer and varies from 1.7 mm.-2.51 mm. in length.

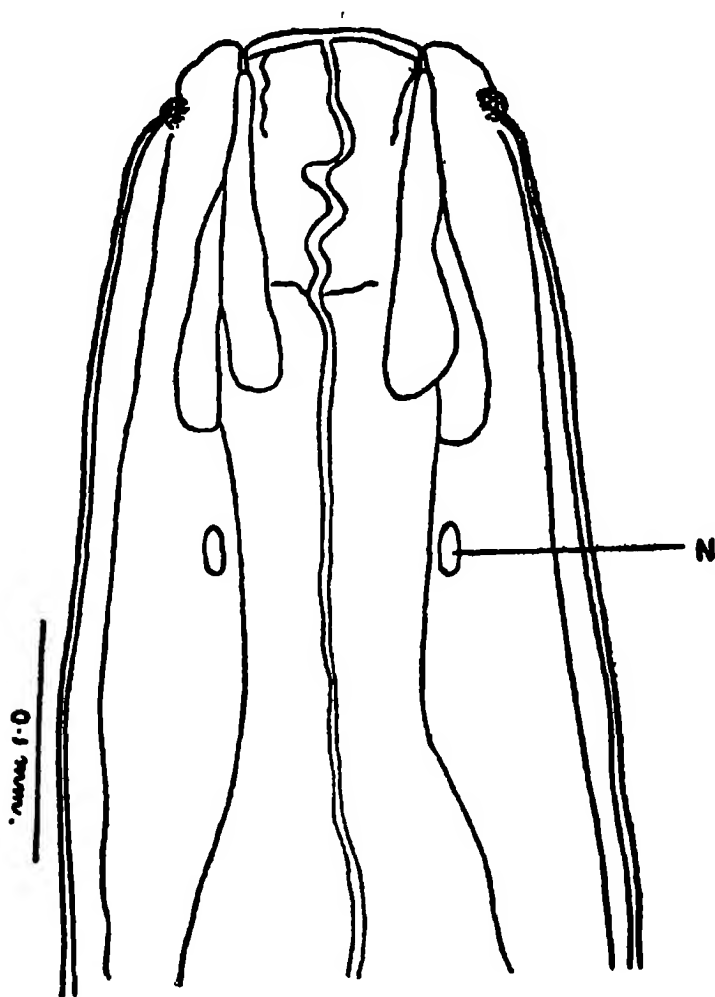


Fig 1

*Diplotriaena acridalhera*

Dorsal view of the anterior end of the male. N—Nerva ring.

In the female the vulva is situated at a distance of 0.454 mm.-0.609 mm. from the anterior end. The vagina is muscular and gradually dilates as it runs posteriorly, the point of bifurcation being situated at a distance of about 2.90 mm. from the vulva in a specimen

measuring 125 mm. The eggs are thick-shelled and measure 0.056 mm.-0.059 mm.  $\times$  0.035 mm.-0.04 mm.

Host—Myna (*Acridotheres tristis tristis*)

Habitat—Body cavity.

Locality—Nagpur (C. P.)

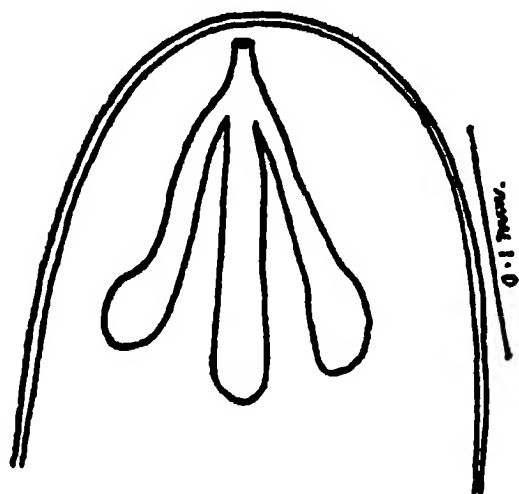


Fig 2

*Diplotriaena acridotheri*

Lateral view of the anterior end of the male.

#### DIPLOTRIAENA NAGPURENSIS N SP

A single male worm of this species was found among the worms belonging to the species *D. acridotheres*. It could easily be marked out from the rest on account of its concave anterior end and the projecting tridents.

The total length of the worm is 33.95 mm. with a maximum thickness of about 0.591 mm. The tridents measure 0.165 mm. Their anterior end is truncated and projects beyond the cuticle of the anterior end of the worm. In the dorsal view the anterior extremity shows a forwardly directed concavity with the tridents on each side of it. The oesophagus is very long and as usual is divided into a short anterior portion, measuring 0.272 mm. and a much larger posterior one with a length of 7.178 mm. The nerve ring is situa-

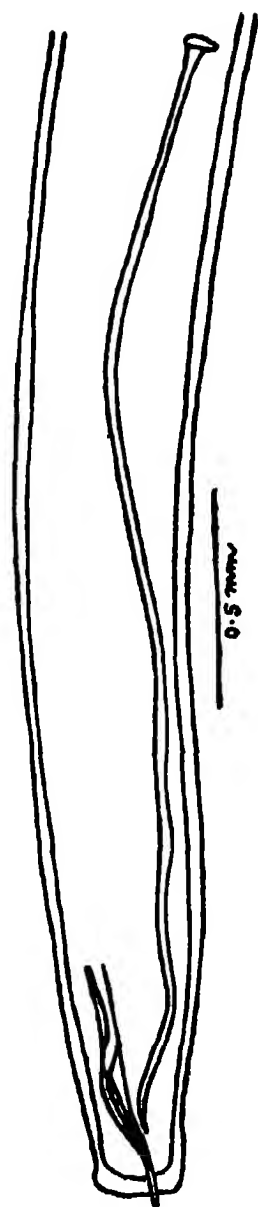


Fig 3

*Diplotriaena acridotheri*

Posterior end of the male to show the epicules. Ventral view.

ted at 0.2 mm. from the anterior end and encircles the first portion of the oesophagus.

The posterior end appears round in lateral view, but when seen from the ventral side, it is truncated. No caudal papillae could be

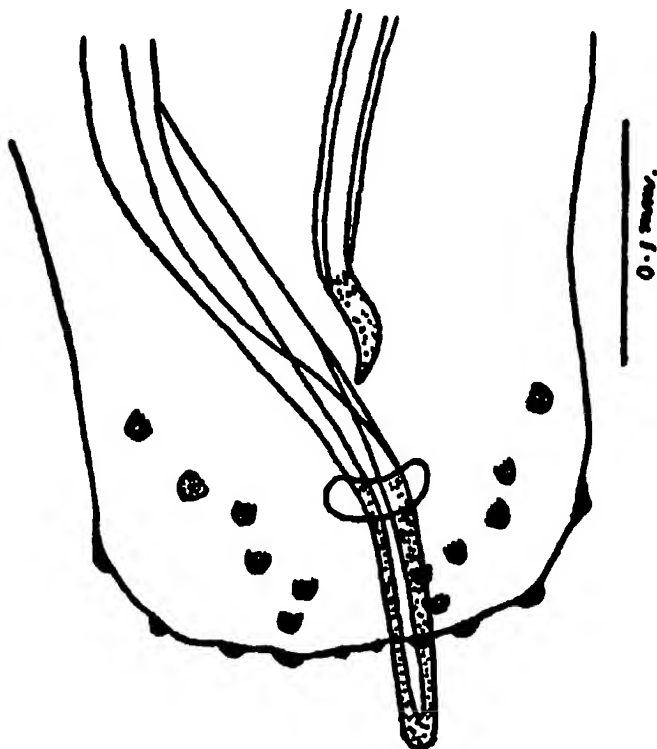


Fig 4

*Diplotrissina acridolheri*

Tail of the male under higher magnification showing the caudal papillae and the ends of Spicules. Ventral view.

made out. The cuticle of the postanal as well as some portion of the preanal region, is granular. The cloaca and the lips of the anal aperture are supplied with muscles which are inserted on cuticular thickenings. The appearance presented by the tail is like a network of muscles with granular interstices. The spicules are unequal and dissimilar. The right one is spirally coiled and measures 0.5 mm. while the left is 2.1 mm. in length.

This worm resembles *D. pungens* (Schneider, 1866) and *D. wroociana* Maplestone, 1931, in certain characters. However, it possesses others which distinguish it from both these species. In

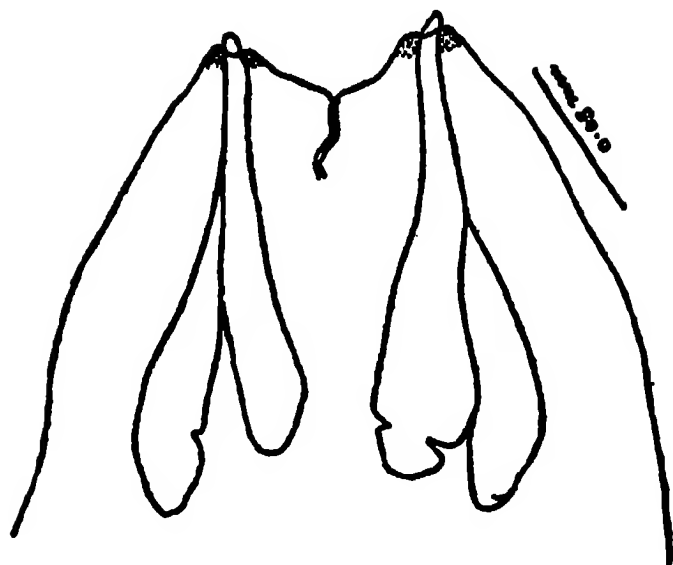


Fig 5  
*Diplotriaena nagpurensis*  
Dorsal view of the anterior end of the male

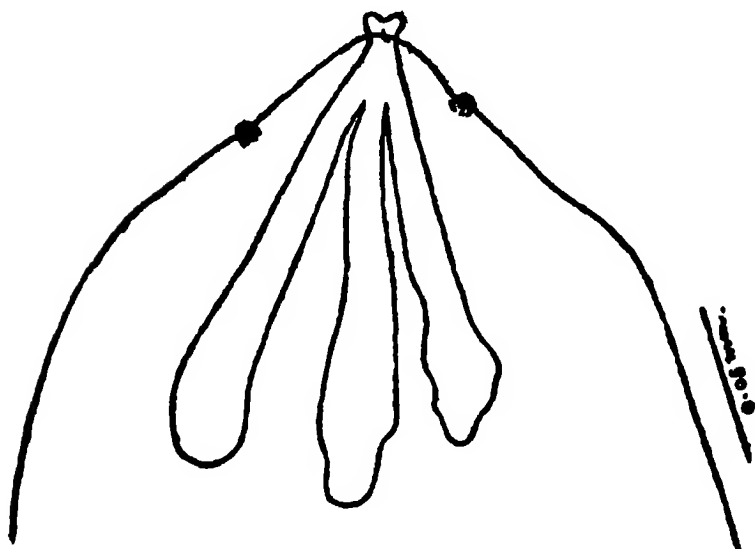


Fig. 6  
*Diplotriaena nagpurensis*  
Lateral view of the anterior end of the male.

*D. pungens* the trident measures 0.25 mm.-0.27 mm.; it is only 0.165 mm. in the present species. The tridents in *D. nagpurensis* protrude beyond the anterior end as in *D. pungens* but the lip-like elevations which are present in the latter species are not present in the former. Moreover in *D. nagpurensis* the anterior end of the

trident is distinctly truncate and forms a slight concavity when viewed laterally. The oesophagus and both the spicules are distinctly smaller in *D. pungens* than these structures found in *D. nagpurensis*. According to Schneider's observations *D. pungens* possesses seven pairs of caudal papillae in the male. Boulenger (1928) could observe only three postanal pairs in the single specimen at his disposal. In *D. nagpurensis* no caudal papillae are present in the male. This would show that *D. nagpurensis* is quite distinct from *D. pungens*.

*D. urocissae* is comparatively a much smaller worm than *D. nagpurensis*. Though in *D. urocissae* the tridents project beyond the cuticle of the anterior end just as they do in *D. nagpurensis*, their anterior ends are sharp and not truncated as in the latter species. Again, there are two pairs of caudal papillae in the male of *D. urocissae*, while there are none in *D. nagpurensis*. Thus it would be seen that *D. nagpurensis* is quite distinct from *D. urocissae*.

Host—Myna (*Acridotheres tristis tristis*)

Habitat—Body cavity

Locality—Nagpur (C. P.).

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*Diplotruaena nagpurensis*  
Caudal end of the male.  
Ventral view.
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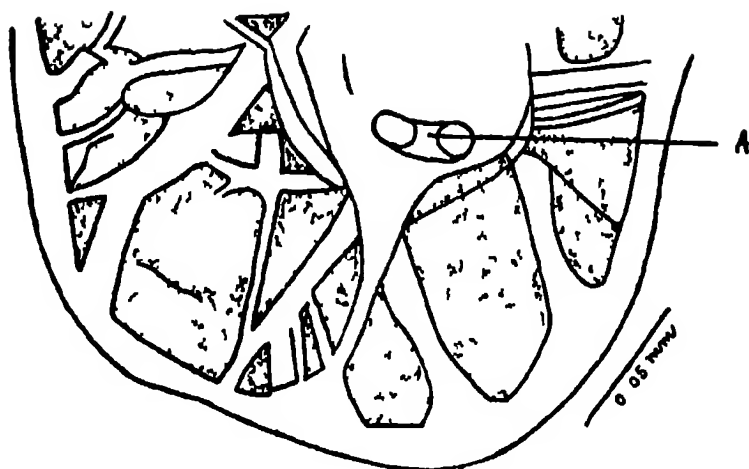


Fig 8

*Diplotriaena nagpurensis*

Tail of the male under higher magnification to show the musculature

A—Anal aperture

# A REPORT ON THE STUDY OF " BLOOD PRESSURE" OF INDIANS IN BOMBAY

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During the past decade or two, the importance of sphygmomanometric measurements has increased to such an extent that to-day it is considered a necessity to estimate the blood pressure as a matter of routine either in the consulting room or at the bedside. The technique of measuring the blood pressure has been so simplified by the introduction of the auscultatory method that it comes within the scope of every general practitioner to make a fairly accurate estimate of the same. Its value from the points of view of diagnosis and prognosis cannot be ignored.

To understand the proper significance of an individual's blood pressure reading in any pathological condition, it is essential to have a definite idea of the normal range of variations under physiological conditions. A good deal of work has been done in other countries on normal blood-pressure and the extent and nature of departure from the normal in various pathological conditions. But unfortunately no such ground work has been done as regards the people of this country. The only reference that we have been able to find is in the work of McCay on the systolic blood pressure of Hindus of Calcutta. The work of Cadbury among Chinese students at Canton and of other observers among people in semi-tropical places suggests that the blood pressure of Indians ought to be lower than that of people residing in more temperate climates. It is with a view to have an idea of the blood pressure and its variations in physiological states under the peculiar environments in India ( Bombay ) that this investigation was taken in hand. An attempt has been made to give a statistical treatment to the data collected from the materials at our disposal with a view to getting a better understanding of the causes responsible for its variations. The blood pressure in cases of Pneumonia was also studied from the materials available in the medical wards of the K. E.

M. Hospital; but this will form the subject of another paper. The work was started at the end of September 1930 and was brought to a close in October 1932. During this period the blood pressure of 1,302 persons was measured. Of these 1,012 were Hindus, 108 were Christians, 113 Parsis, 64 Mohamedans and 5 Jews.

#### *Materials and the method*

The basal blood pressure, i. e. the blood pressure under basal conditions of metabolism was investigated among those of the students, resident medical officers, nurses and the clerical staff, residing on the premises of the group of hospitals in Parel. The blood pressure during working hours was studied in addition, amongst school children attending Dadar schools and amongst clerks of the Municipal Head Office and among students of the Ismail College, Andheri.

Throughout our investigations we have adopted the horizontal position (recumbent posture) without a pillow or with a low pillow under the head. The subjects were allowed to lie down for about five minutes on the couch during which period a record of the name, sex, relevant personal history, family history and habits (especially as regards food, alcohol and tobacco) was made in order to allow time for the subjects to get over the nervousness and become familiar to the examiner before the readings were taken.

A mercury manometer graduated in Mms of Hg. with a standard 12 c. m. arm cuff was used. The pulse rate was counted for half minutes until two countings tallied. Three blood-pressure readings were taken and the average of the last two readings was recorded. The systolic blood pressure was read at the appearance of first clear sound and the diastolic at the point of transition between the 3rd phase of sharp clear sounds and the 4th phase of muffling of the sounds. A record of the height and weight was obtained and the urine of the subjects was examined for albumin and sugar.

We have omitted from consideration those cases which presented any cardiovascular abnormality (except sinus arrhythmia) and those cases which showed presence of albumin or sugar in the urine. In our series, 12.25% of school children between 6 and 20 years of age showed respiratory or sinus arrhythmia. The urine of 4 out of 522 children showed a faint reduction with Fehling's solution but the problem was not investigated further. Three children gave positive tests for albumin by the heat and sulpho-salicylic acid tests.

#### RESULTS.

##### *Blood Pressure of Hindus*

The average systolic pressure of Hindu boys between 5 and 9 years of age was found to be 84.2 mms. For boys between 10 and 19 years of age, it was found to be 93.4 mms. For adults of 20 to 29



years, 30 to 39 years and 40 to 49 years it was found to be 114.5, 120.8 and 116.5 mms. respectively. The systolic blood pressure of all the adult age groups mentioned above, does not show a fluctuation greater than can be accounted for by chance variation alone, and here we agree with Wing Commander Treadgold that "age between 18 and 40 and proportionate height and weight have little effect on blood pressure". The majority of this group (Hindus) were vegetarians and teetotalers. Those of them who styled themselves non-vegetarians had in addition to the vegetarian diet a few eggs and few ounces of meat or fish once or twice a week. All the medical students who took a fair amount of exercise fall in the age group 20 and 29 years whilst in the higher age group are included clerks and others following a sedentary occupation. The results are arranged in Table I. Similar figures from English and American sources are given in Table IIIa. The figures found by us for the various age groups are considerably below those given by those authors. Compared with Americans our subjects showed a difference of 14.9 mms. in the systolic pressure. McCay at Calcutta found the systolic blood pressure of Hindus to vary between 83 and 110 mms., the average being a little over 100 mms. In another series of observations he found the averages to be more or less the same. Our figures as compared to McCay's are slightly higher both as regards the average as well as the range of variation. Cadbury working with Cantonese students found the averages which are given below :—

<i>Cadbury</i>			<i>Our work</i>		
14 years.	{ Systolic.	83 mms.	10 to 19 years.	{ Systolic.	93.4 mms.
	{ Diastolic.	51 "		{ Diastolic.	56.1 "
	{ Pulse.	31 "		{ Pulse.	33.48 "
15 to 20 years.	{ Systolic.	101 mms.			
	{ Diastolic	62 "			
	{ Pulse.	39 "			
21 to 30 years.	{ Systolic.	101 mms.	21 to 30 years.	{ Systolic.	114.52 mms.
	{ Diastolic.	68 "		{ Diastolic.	73.23 "
	{ Pulse.	36 "		{ Pulse.	44.32 "

It will be noticed that our figures are higher than those of Cadbury. He found that 60% of his subjects had blood pressure ranging between 90 and 110 mms., whilst 57.4% of our subjects had a systolic blood pressure ranging between 90 and 119 mms. 81.8% of the Hindu nurses examined had a systolic blood pressure ranging between 90 and 119 mms. It will be noticed that there were several cases that showed a systolic pressure of over 130 mm. They form 0.26% in the age group 10 to 19 years, 10.9% in the age group 20 to 29, 22.2% in the age group 30 to 39 years and 18.7% in the age group 40 to 49 years. The subjects who had blood pressures below average were

found to have no symptoms and were as fit as others, showing that "hypotension, even when systolic pressure is below 100 mms., can be present in good health."

The results of the *diastolic pressure* readings are tabulated in Table II. Here again we find that our figures are lower by about 10 mms. than the figures given for Americans. In McCay's work we find no reference to diastolic pressure. Our figures are a trifle higher than the figures of Cadbury for Chinese students. About 76% of our subjects had diastolic pressures between 60 and 79 mms. Nearly 20% had diastolic pressure below average. The average figures show little variation in the age groups above 20 years.

*Pulse pressure* readings are tabulated in Table III. The average pulse pressure for adults was found to be 44 mms. In children it is slightly lower than in adults and slowly increases with age. It rises in proportion to the height of systolic blood pressure as will be noticed below.

#### *Body Weight and Blood Pressure*

The blood pressure in the age group 5 to 19 years has been tabulated in Tables IV, V and VI. The systolic blood pressure shows a steady increase with increase in body weight. The same is true for the diastolic pressure also though it does not show the same amount of increase as the systolic. Consequently we find that the pulse pressure rises, the difference being due more to the rising systolic pressure than to the diastolic, a fact that has been noticed by other observers before. Table VII shows a comparison between the results of Michael and of Cadbury and of ourselves. Our figures though higher than Cadbury's are considerably lower than the figures given by American authors.

The relation between body height and blood pressure of the age group 9 to 19 years is shown in Table VIII, and Table VIII (a) shows similar figures for American subjects. The systolic blood pressure rises gradually as the height increases. Though the relative increase is the same in Indians and in Americans, the absolute figures for the latter are higher by about 10 mms. The diastolic pressure too shows a slight increase with increased height.

#### *Blood Pressure of other communities.*

The systolic and diastolic pressures of Hindu children at Dadar schools were found to be lower than those of the Christian children of the same age and locality. The difference was about 4.7 mms for systolic blood pressure and 10.41 mm. for the diastolic pressure. The Christian boys were comparatively of better physique than the Hindu boys of the same locality. The students of a Parsi school in the Fort were found to have systolic blood pressure about 7 mms. higher than that of the Christian boys. In the medical students of the Seth G. S.

Medical College, the blood pressure of the students of the various communities was approximately the same. The blood pressure of the Mohamedan students of the Ismail College, Andheri, is shown in Table XI, compared with that of the Hindu students of the Medical College. The figures for the systolic pressure are equal to the nearest integer, whilst the diastolic figures in Mohamedans are higher by 3.8 mms. than in Hindus. The conditions of life of both sets of students are more or less the same except perhaps that the medicos have to do a greater amount of work than the students of the other college. The average systolic pressure for both the groups is about 113.3 mms. The problem demands more investigation before final conclusions can be drawn therefrom.

#### *Diet and Blood Pressure.*

The blood pressure of adults of the age group 30 to 50 years has been classified from the point of view of diet in Table XII. The subjects classified as vegetarians in the Table were total abstainers from all animal food except milk. The non-vegetarian diet consisted of a few eggs and a few ounces of meat or fish daily, besides the usual diet consisting mainly of rice, wheat and vegetables. The systolic blood pressure of vegetarians was found to be 112.0 mms. and that of non-vegetarians was found to be 120.0 mms.—a difference of 8 mms. The average diastolic was found to be 78.4 and 76.2 mms. for the non-vegetarians and the vegetarians respectively—difference of 2.2 mms. All these subjects were clerks employed in the various departments of the Bombay Municipal Head Office having the same conditions of life as regards work, exercise, etc.

#### *Occupation and Blood Pressure.*

Table XIII shows the blood pressure of clerks and labour staff of different age groups compared. The labour staff of the hospital consisted of ward boys and gardeners. Most of the subjects of the labour staff had habits of drinking toddy or country liquor and of chewing tobacco, while the number of people who had such habits among the clerical staff was practically nil. The systolic blood pressure of clerks of age between 20 and 29 years was found to be higher by about 4 mms. while that of the clerks of age between 30 and 39 years of age was found to be 7.3 mms. higher than that of the labour staff of the same age. The members of the labour staff had to do a greater amount of manual labour than the clerks. Perhaps the higher figures for the clerks can be accounted for by the sedentary habits combined with inadequate opportunities for physical exercise and worries incidental to their work and to their status in life.

#### *Basal Blood Pressure.*

This group consisted of male medical students and female nurses

of the King Edward VII Memorial Hospital. The students were between 20 and 28 years of age while nurses were between 18 and 28 years. The blood pressure was taken between 5-30 a.m. and 6-30 a.m. while the subjects were still in bed. In comparison the blood pressure was again taken at 4 p.m. after they had been working since 8 a.m. The average basal systolic pressure of male students was 103.53 mms. and was 7 mms. lower than that taken during working hours. The working hour diastolic pressure showed a rise of 2.5 mms. from basal diastolic pressure. In the nurses the average basal systolic pressure was found to be 95.6 mms.—lower by about 9.2 mms. than the working hour systolic pressure. The working hour diastolic pressure showed an increase of 5.5 mms. from the basal diastolic pressure. The difference between the working hour blood pressure and the basal blood pressure is greater in the females than in the males. The basal blood pressure of Hindu nurses was found to be higher than that of Christian nurses, which might be due to the greater emotional tone noticed in the former.

#### *Arteriosclerosis*

Another interesting fact brought out in this investigation was the frequency of arteriosclerosis in children as judged by the thickening and palpability of the walls of the radial and brachial arteries. The relative frequency in different communities is shown in Table XV. The average blood pressure of the cases of arteriosclerosis we came across during the course of our investigations is shown in Table XV. There seems to be no definite relation between arteriosclerosis and high blood pressure in these cases. But here again the number of subjects is not sufficient to warrant any conclusions.

#### *Pulse rate.*

The average pulse rate for Hindu school children at Dadar between 5 and 9 years of age was found to be 86.5 per minute. Between 10 and 19 years it was found to be 82.5 per minute. For adults it was found to be on an average 75 per minute. The results are tabulated in Table XVI.

The basal pulse rate of students (males) between 20 and 28 years was found to be 63.7 per minute and the working hour pulse rate taken at 4 p.m. was 73.19. Among the nurses between 18 and 28 years it was 70.9 and that taken during working hours was found to be 75.45. The pulse rate of females under basal as well as under working hour conditions was higher than in males.

#### *Summary.*

1 The systolic blood pressure of Hindus in Bombay is lower by about 10 to 15 mms. than that of Americans or Englishmen. The diastolic is lower by about 5 mms.

2. The relative proportion between body weight, body height and blood pressure is approximately the same in Indians, as in Americans. "Age has little influence on blood pressure among adults of proportionate height and weight." (Ref. 11).

3. The average basal systolic blood pressure is lower by about 7.14 mms. than the systolic blood pressure taken under working conditions in males and 9.2 mms. in females. The diastolic blood pressure shows smaller variation.

4. The blood pressure of Christian and Parsi children is higher than that of Hindu children but the problem requires further investigation before definite conclusions can be drawn.

5. The systolic blood pressure of clerks and intellectuals is higher than that of manual workers

6. The blood pressure of people who live on a non-vegetarian diet tends to be higher (by about 8 mms) than those living upon a vegetarian diet

#### *Acknowledgments*

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TABLE I  
*Systolic pressure in Hindus (Males)*

Blood pressure in Mms of Mercury	5 to 9 yrs	10 to 19 years	20 to 29 years	30 to 39 years	40 to 49 years
60-69 Mms	3				
70-79 "	29	31			
80-89 "	56	115			
90-99 ,	22	155	1	2	1
100-109 ,	5	56	16	3	5
110-119 ,		23	25	6	3
120-129 "		10	7	10	4
130-139 "		1	6	5	3
140-149 "					
150-159 ,				1	
Total	115	391	55	27	16
Mean	84.2	93.4	114.52	120.79	116.5
Probable error mean	$\pm 0.5025$	$\pm 0.3411$	$\pm 0.6717$	$\pm 1.658$	$\pm 1.951$
Standard deviation	7.991	10.69	9.309	12.78	11.26
Probable error of standard deviation	$\pm 0.3554$	$\pm 0.2412$	$\pm 0.5980$	$\pm 1.172$	$\pm 1.374$
Co efficient of variation	9.491	10.72	8.130	15.29	9.899
Probable error of co efficient of variation	$\pm 0.4249$	$\pm 0.2614$	$\pm 0.8577$	$\pm 1.435$	$\pm 1.472$
Percentage above 130 Mms		0.26	10.9	22.2	18.75

TABLE II.

*Diastolic blood pressure of Hindus (Males).*

Pressure in Mms. of Hg.	5-9 years	10-19 years.	20-29 years	30-39 years.	40-49 years.
30-39 Mms.	10	8	...	...	.
40-49 "	35	24	.	..	...
50-59 "	40	131		.	...
60-69 "	29	164	15	5	3
70-79 "	1	59	34	11	6
80-89 "	...	5	4	6	7
90-99 "	.	.	2	5	...
100-109 "	..	...	...	...	...
Total	115	391	55	27	16
Mean	52.42	56.10	73.226	78.50	77.00
Probable error of Mean	0.5652	0.6176	0.5630	1.223	3.681
Standard deviation	9.003	18.100	6.255	9.421	21.88
Probable error of standard deviation.	0.4004	0.4367	0.4018	0.8648	2.609
Co-efficient of va- riation. ...	17.18	32.42	8.545	12.00	28.41
Probable error of co-efficient of va- riation. ..	0.7863	0.4512	0.5530	1.118	2.812

TABLE III.

*Pulse pressure of Hindus (males).*

Pressure in Mms. of Hg	5-9 years.	10-19 years.	20-29 years.	30-39 years	40-49 years
10-19 Mms.	3	7	..	.	.
20-29 "	40	138	1	..	..
30-39 "	47	157	21	9	6
40-49 "	22	68	22	13	8
50-59 "	3	19	10	3	1
60-69 "	.	2	1	2	1
Total ...	115	391	55	27	16
Mean.	32.94	33.48	44.32	43.7	44.62
Probable error of Mean	0.5034	0.2945	0.4665	1.048	1.271
Standard deviation	8.004	8.636	5.018	8.074	7.532
Probable error of standard deviation	0.3559	0.2083	0.3298	0.7411	0.8982
Co-efficient of variation. . .	24.3	26.1	11.58	18.49	16.91
Probable error of co efficient of variation. ...	1.596	0.6866	0.7543	1.752	2.067



TABLE III a.

*Blood pressure of Europeans and Americans.  
Average blood pressure (in Mms. of Hg.) Comparison  
of the results of three investigators*

	Males.		Females.	
	Systolic.	Diastolic.	Systolic.	Diastolic.
<b>Age 15-29 years.</b>				
Alvarez	129.4	...	126.3	83.7
Dunham.	122.0	76.0	...	...
Symmonds.	123.4	79.8	120.6	78.4
<b>Age 30-39 years.</b>				
Alvarez.	130.4	...	129.8	86.1
Dunham.	123.0	77.0	...	...
Symmonds.	124.3	82.0	122.4	80.9
<b>Age 40-49 years.</b>				
Alvarez	133.4	...	141.4	91.4
Dunham.	127.0	81.0	...	...
Symmonds.	127.3	84.3	126.9	84.1
<b>Age 50-59 years</b>				
Alvarez.	144.1	...	157.3	96.1
Symmonds.	131.2	86.5	132.1	87.3
<b>Age 60 Years and over.</b>				
Dunham.	134.1	83.0	...	...
Symmonds	131.2	86.6	135.5	89.8
<b>All ages.</b>				
Alvarez.	134.7	...	137.6	89.8
Dunham.	125.0	78.1	...	...
Symmonds.	125.3	82.1	122.8	80.5
Halls Daily.	127.0	84.0	123.0	81.0

TABLE IV  
*Comparison of systolic blood pressure and weight*  
 Age group 5 to 19 years (males).

Pressure in Mms.	lbs. 40-49	lbs. 50-59	lbs. 60-69	lbs. 70-79	lbs. 80-89	lbs. 90-99	lbs. 100-109	lbs. 110-119	lbs. 120-129	lbs. 130-139	All weight
60-69		1	1								1
70-79	24	14	22	7	2	2					39
80-89	62	55	46	26	12	12	6	1			150
90-99	37	65	17	12	14	21	9	15	2		205
100-109	11	21	2	4	15	11	13	16	6	4	122
110-119	3	5	3	1	3	4	4	3	5	2	79
120-129		1					1	1	5	2	26
130-139									0	1	8
140-149											2
Total	137	162	91	50	46	50	33	36	18	9	632
Mean.	87.1	91.29	95.16	97.7	105.59	105.1	110.26	111.22	111.72	114.5	96.86
Probable error of mean.	0.5079	0.5772	0.7257	0.3173	0.9572	0.8585	0.254	0.8186	1.054	7.193	0.2705
Standard deviation.	8.8	10.89	10.27	8.35	9.625	9.258	10.65	7.264	9.458	10.12	10.07
Probable error of standard deviation.	0.3591	0.4032	0.5133	0.2244	0.6769	0.3941	0.8886	0.5774	1.068	5.087	0.1913
Co-efficient of variation.	10.05	11.93	10.78	8.55	9.13	8.80	9.658	6.553	8.474	8.835	10.4
Probable error of co-efficient of variation.	0.4175	0.4545	0.5455	0.5902	0.6476	0.7537	0.8095	0.5217	0.9752	4.559	0.1995

TABLE V.  
*Comparison of diastolic pressure and weight (Age 5 to 19 years.) Males.*

Pressure.	lbs. 40-49	lbs. 50-59	lbs. 60-69	lbs. 70-79	lbs. 80-89	lbs. 90-99	lbs. 100-109	lbs. 110-119	lbs. 120-129	lbs. 130-139	All weights
30-39 Mms											
40-49 "	4	5	2		"					..	9
50-59 "	26	15	28	13	1	6	1	1		..	44
60-69 "	49	57	44	25	3	23	12	7	6	...	158
70-79 "	49	66	16	10	23	20	18	23	11	2	257
80-89 "	9	19	1	2	17	1	1	5	1	6	149
90-99 "	.		.		2	.	1		1	1	13
100-109 "	.					.	1		.	..	1
	137	162	91	50	46	50	33	36	18	9	632
Mean.	56.9	59.36	62.95	64.57	66.97	67.7	71.47	69.51	72.2	73.6	63.06
Probable error of Mean.	0.5125	0.4684	0.5037	0.9259	0.6988	0.9229	0.9191	1.451	1.016	2.688	0.2809
Standard deviation.	8.894	8.83	7.125	9.374	7.028	9.078	7.827	12.90	6.395	3.738	10.46
Probable error of standard deviation.	0.3624	0.3562	0.3562	0.8418	0.4942	0.8445	0.6500	1.026	0.7888	1.879	0.1966
Co-efficient of variation.	15.63	14.89	11.32	9.799	10.49	9.904	10.95	18.57	8.857	5.078	16.59
Probable error of co-efficient of variation.	0.6539	0.5702	0.5733	0.8561	0.9391	0.9084	0.9202	1.528	1.071	3.147	0.3311

TABLE VI.  
*Comparison of pulse pressure and weight of boys (age between 5 and 19 years.)*

Pressure.	lbs. 40-49	lbs. 50-59.	lbs. 60-69	lbs. 70-79	lbs. 80-89	lbs. 90-99	lbs. 100-109	lbs. 110-119	lbs. 120-129	lbs. 130-139	All weights.
10-19 Mms.	3	4		1							8
20-29 "	56	60	25	15	6	9	5	3	1	1	181
30-39 "	57	71	46	20	19	24	14	16	5	1	273
40-49 "	17	24	17	12	16	13	12	16	10	6	143
50-59 "	4	3	3	1	4	4	2	1	2	1	25
60-69 "				1	1						2
Total	137	162	91	50	46	50	33	36	18	9	632
Mean.	32.7	32.16	34.2	34.5	39.06	36.9	37.84	38.67	42.6	42.2	31.37
Probable error of mean.	0.4395	0.3934	0.5047	0.8509	0.6829	0.7502	0.8843	0.6955	1.066	5.337	0.3665
Standard deviation.	7.628	7.418	7.139	8.921	6.868	7.865	7.541	6.186	6.701	7.489	13.65
Probable error of standard deviation.	0.3109	0.2783	0.3569	0.6077	0.4829	0.5306	0.6262	0.4918	0.7539	3.774	0.2562
Co-efficient of variation.	23.3	23.1	20.87	25.86	17.58	21.31	19.93	16.00	15.74	17.83	43.7
Probable error of co-efficient of variation.	1.001	0.9103	1.092	1.860	1.274	1.502	1.720	1.307	1.805	9.143	0.8306

TABLE NO VII.

*Table showing the relation of blood pressure to body weight of different authors.*

Body weight in lbs.	Systolic pressure.			Diastolic pressure.		Pulse pressure.	
	Michael American.	Cadbury Chinese.	Indian	Cadbury Chinese.	Indian.	Cadbury Chinese.	Indian
20-30		60		30		30	.
30-40	95	81		51	..	29	
40-50	100	83	87 1	51	56.9	32	32.7
50-60	107	87	91.29	55	59.36	32	32.16
60-70	112	94	95.16	60	62.96	34	34.2
70-80	116	96	97.7	59	64.57	37	34.5
80-90	122	100	105.59	60	66.97	40	39.06
90-100	126	101	105.1	63	67.7	32	36.9
100-110	.	104	110.26	64	71.47	40	37.84
110-120	...	106	111.22	65	69.51	41	38.67
120-130	.	106	111.72	66	72.2	41	42.6
130-140	.		114.50			.	42.2

TABLE VIII.

*Comparison of body height and blood pressure (Males).*

Height.	No. examined.	Systolic pressure	Diastolic pressure.	Pulse pressure.
		Mms.	Mms.	Mms.
3'-6" to 4'-0"	98	85.3±0.5384	52.7±0.6657	32.7±0.6132
4'-4" to 4'-6"	255	88.3±0.4592	60.3±0.6422	32.2±0.4145
4'-6" to 5'-0"	102	97.9±0.7964	66.1±0.5829	34.6±0.5599
5'-0" to 5'-6"	135	108.6±0.5899	71.6±0.4335	39.6±0.4096
5'-6" to 5'-9"	33	112.4±1.024	72.3±0.7930	39.9±0.9494

TABLE VIII A

*Comparison of blood pressure and body height of American children (Michaels), with Indian Children examined during the course of the present enquiry*

Height.	Systolic pressure.	
	American Children	Indian Children
3'-6" to 4'-0"	99 Mms. of Hg	85.3 Mms.
4'-0" to 4'-3"	109 "	87.5 "
4'-3" to 4'-6"	112 "	93.1 "
4'-6" to 4'-9"	118 "	94.3 "
4'-9" to 5'-0"	120 "	100.3 "
5 feet and over.	125 "	108.0 "

TABLE IX.

*Comparison of basal blood pressure and blood pressure during working hours (Males 52. Ages 20-28)*

	Basal blood pressure.	Evening.	Difference
Systolic pressure	103.53 $\pm$ 4867 Mms.	110.64 $\pm$ 1361 Mms.	7.14 $\pm$ 1.446 Mms.
Diastolic "	70.0 $\pm$ 4538 "	72.5 $\pm$ 7723 "	2.5 $\pm$ 0.8984 "

*(Females—35. Ages 19-24)*

	Basal blood pressure	Evening	Difference.
Systolic.	95.64 $\pm$ 1.063 Mms.	104.83 $\pm$ 0.4735 Mms.	9.21 $\pm$ 1.154 Mms
Diastolic.	65.49 $\pm$ 0.9401 "	70.0 $\pm$ 0.4942 Mms.	5.51 $\pm$ 1.061 "

The basal blood pressure was taken in the morning after rest during the previous night and before the subjects had got up and stirred out of bed. The evening blood pressure was taken between 4 p. m. and 5 p. m. on the same day and where it was not possible it was measured between 4 p. m. and 5 p. m. the next day

TABLE NO. X.

*Blood pressure of Hindus, Christians and Parsis (males).  
5 to 19 years*

	Hindus.	Christians.	Parsis.
No. examined.	391	100	100.
Systolic pressure.	Mms. $93.4 \pm 0.3411$	Mms. $98.1 \pm 0.8726$	Mms. $107.9 \pm 0.7017$
Diastolic    "	$56.1 \pm 0.6176$	$66.5 \pm 0.4955$	$71.0 \pm 0.4545$
Pulse        "	$33.48 \pm 0.2945$	$36.0 \pm 0.4343$	$36.4 \pm 0.5811$

TABLE NO. XI.

*Blood pressure of Mahomedan students (of Ismail College, Andheri)  
and Hindu students (of the Seth G.S.M. College, Bombay).  
20-29 (Males).*

No. examined.	Mahomedans. 28	Hindus. 47
Systolic pressure.	113.4 Mms. of Mg.	113.0 Mms.
Diastolic    "	78.3    "    "	74.5    "
Pulse        "	35.1    "    "	39.5    "

TABLE XII.

*Comparison of blood pressure of vegetarians and non-vegetarians  
(males) Municipal clerical staff (30-50 years).*

No. examined.	Vegetarians 46	Non-vegetarians. 35
Average systolic pressure.	$112.0 \pm 1.32$ Mms.	$120.0 \pm 1.049$ Mms.
"   diastolic   "	$78.4 \pm 0.3214$ "	$76.2 \pm 0.6116$ "
"   pulse       "	$48.8 \pm 0.3214$ "	$46.0 \pm 0.9572$ "

TABLE XIII.

*Comparison of blood pressure of clerical and labour staff.*

(Males.)

No. examined.	Age 20 to 29 years.		Age 30 to 39 years.	
	Clerks 55	Labour staff 41	Clerks 27	Labour staff 29
Systolic pressure.	Mms 114.1±0.6717	Mms 111.82±1.023	Mms 120.79±1.668	Mms 113.47±1.477
Diastolic ..	73.26±0.5630	69.77±1.039	78.5 ±1.233	78.78±0.6993
Pulse ..	44.32±0.4665	38.16±1.921	43.7 ±1.048	37.95±0.9695

TABLE XIV.

*Blood pressure in Arteriosclerosis.*

Age.	No. examined.	Average systolic pressure.	Average diastolic.
10 to 14 Yrs.	15	103.0	64.0
15 to 19 "	19	124.0	72.0
20 to 24 "	3	125.0	77.0
25 to 29 "	1	120.0	76.0
30 to 34 "	6	112.0	77.0
35 to 39 "	3	118.0	79.0
40 to 49 "	1	115.0	81.0
50 to 59 "	..	..	..
60 to 69 "	1	130.0	74.0

		Arteriosclerosis in children.
Community.	No. examined.	No. of arteriosclerotic subjects.
Hindus	520	28
Christians	100	6
Parsis	100	2



TABLE KV.

*Comparison of average blood pressure & pulse rate of Christian and Hindu nurses. ( Age between 18 and 51 yrs. ) Majority 20-35 yrs.*

Caste.	No. examined.	Systolic pressure.	Diastolic pressure.	Pulse rate.
Christian.	74	109.2	79.3	83.1
Hindu.	33	111.78	79.04	87.7

TABLE XVI.

*Pulse rate of men ( working hours. )*

Age.	5 to 9 yrs.	10 to 19 yrs.	20 to 29 yrs.	30 to 39 yrs.	40 to 49 yrs.
No. examined.	115	391	67	28	19
Pulse rate	$86.5 \pm 0.3711$	$82.5 \pm 0.3319$	$74.69 \pm 0.6159$	$77 \pm 0.2315$	$76.6 \pm 1.309$

TABLE XVII.

*Frequency distribution of systolic blood pressure of Nurses ( between 19 and 29 years ).*

	Number examined.	Christians, Indian Christian, Anglo-Indians.	Hindus.
90-99 Mms.	5	5	...
100-109 Mms.	31	20	11
110-119 "	24	17	7
120-129 "	8	5	3
130-139 "	3	2	1
140-149 "	1	...	...
	71	49	22

TABLE XVIII.

*Ranges of variation of blood pressure in young adults (20-29).*

		Women		Men	
		Basal	Working hours	Basal	Working hours
Systolic.	Max.	120	127 Mms.	122 Mms.	134 Mms.
	Minm.	79	87 "	85 "	90 "
Diastolic.	Maxm.	87	86 "	84 "	84 "
	Minm.	53	54 "	58 "	64 "

TABLE XIX.

*Blood pressure and weight in men of age between 25-40 years (Municipal Clerks)*

Weight in lbs.	No. examined	Systolic pressure	Diastolic pressure
95-99 lbs.	4	107.5 Mms.	69.35 Mms.
100-109 "	7	116.7 "	73.85 "
110-119 "	11	112.45 "	74.72 "
120-129 "	13	113.3 "	70.4 "
130-139 "	10	120.1 "	76.3 "
140-149 "	8	121.0 "	80.8 "
150-159 "	7	123.7 "	82.57 "

TABLE XX.

*Blood pressure and height in men of age between 25-45 years (Municipal clerks).*

Height in inches.	Number examined.	Systolic pressure.	Diastolic pressure.
55-59	1	105 Mms. of Hg.	74 Mms.
60-62	9	118.7 "	74 "
63-65	24	114.7 "	75.3 "
66-68	23	114.3 "	70.43 "
69-71	5	124 "	83 "

## Reviews

*Practical Anatomy by Six Teachers*, edited by E. P. STIBBE, F. R. C. S (Edward Arnold & Co.) London, 1932, 30s. net.

This book is a useful addition to the current text-books on Practical Anatomy, and is designed specially to meet the requirements of students working for M. B. B. S. examinations in this subject. As stated in the Preface, it is intended to replace the Practical Anatomy of Professors Parsons and Wright, who have generously permitted every use to be made of their original text and illustrations. The six teachers, who have contributed different sections, are Professor W Wright of the London Hospital Medical School (The Abdomen and Pelvis), Professor T. Yeates of the Middlesex Hospital Medical School (The Thorax), Professor J. S. B. Stopford of the University of Manchester (The Central Nervous System), Professor S. E. Whitnall of the McGill University, Montreal (The Orbit, Eye, and Ear), Professor Mary F. Lucas Keene of the London School of Medicine for Women (the Head and Neck), and Mr. E. P. Stubbe of the London Hospital Medical School (The Limbs). The hints regarding the dissection are concise and practical. In studying each part, the instructions are to study the Skeleton first, then the surface markings and finally dissections. This is how it should be. The Skin incisions, and subsequent steps in the dissection are clearly put, and described in their logical sequence, and well illustrated by numerous diagrams (an important feature of the book). It must prove a difficult task for any author to judge as to how much theoretical descriptions of parts should be included in a practical handbook such as this. This difficulty is successfully overcome, for the book is the outcome of mature teaching experience of a number of distinguished anatomists, and the students will find it a real aid in the Dissection-Room.

S. L. BHATIA

*Text Book of Pathology*. By ROBERT MUIR, F. R. S., Third Edition. (Edward Arnold & Co.) London, 1933, 35s. net.

The third edition of the Text Book of Pathology by Professor Robert Muir has been published four years after its predecessor. It was

first published in 1924 and reprinted in 1924, 1926 and 1927; the second edition came out in 1929, and reprints again in 1930 and 1932. This speaks volumes regarding its immense popularity as a guide to the students of Pathology. In the new edition the general plan remains the same, but numerous additions have been made, bringing the subject matter up-to-date. This book has a scientific and practical outlook and caters specially for the requirements of the student of medicine. Stress has been laid throughout on the fact that disease processes are disturbances of function and structure. It deals specially with the anatomical (gross and microscopic) aspect of Pathological processes, although the biochemical aspect is not ignored, but the student must supplement this by reference to other books. The same applies to the Pathology of Tropical Disease. The book contains sound teaching and maintains a good balance, and the student will turn to it with delight to acquire the fundamentals of the science of Pathology.

S. L. BRATIA

*An Outline of Immunity.* By W. W. C. TOPLEY, (Arnold & Co.) London, 1933

We undertook the review of this book with the same apprehension that the author expresses about his writing a new text-book on Immunology. A text-book it looks, indeed, in title and size; but even a superficial inspection of the contents suggests it to be something better. To attempt to write at this stage of that science is daring enough; and it was for this reason that the volume attracted our attention. On the other hand, we sometimes have wasted so much time, when we have been "caught" by pretentious monographs which are merely chapters of text-books, that a feeling, at the commencement, of distrust towards a book openly called an 'Outline' was explicable. However, the reading of the first few pages gave us at once that pleasant feeling of being in the company of a master. The book is very cleverly written. A man just initiated in the knowledge of immunity may think that it contains nothing new. But the fact is that much more than the outlined phenomena is given by the scientific arrangement of the matter, and both in the selection and elimination of the material, in the correlation of the facts and in the very original and illuminating remarks, the personality of the author, overshadowing solutions, is manifest enough.

Right at the outset, for instance, he says (p. 3) "Another important change that the immunologist makes in the clinical and epidemiological picture is in regard to the character and extent of the

association between any given parasite and the host species that it infects. He finds that the real range of interaction includes states of equilibrium in which the host shows no overt signs of disease. Whether we call all these conditions latent infections, or refer to many of the hosts as healthy carriers, matters little." As pertinent to similar ideas developed in that chapter, I may mention the tendency to generalize parallelisms and relationships, where perhaps only local phenomena with peculiar conditions are involved. *Webster and Clow* (J. Exp. Med. 58, 465, 1933) have shown that in the case of the intraperitoneal virulence of the pneumococcus in mice, a high peritoneal pathogenicity may be, and often is, accompanied by an almost total lack of nasal infectivity. There may be parallelism between nasal virulence and the tendency of the pneumococcus to set up carrier conditions, but usually there is lack of parallelism with virulence as determined by the intraperitoneal method, used as the test of infectivity.

Even in the descriptive portions, the author manages to insert a stimulating remark, as when speaking of susceptibility to diphtheria, he asks (p. 280). "Is a point reached in natural immunization at which a person resists carrier infection in the clinical sense? Can we grade our Schick-immunes as we grade our Schick susceptibles, putting at the lower end of the scale those who have just attained to the Schick level of immunity and at the upper end of the scale those who are so resistant that virulent diphtheria bacilli are unable to gain lodgement in their throats?"

Sometimes we find the author, we would not say cautious to the extreme, because great caution is necessary in the treatment of this subject, but less favourably disposed to accept results which have as good a claim for acceptance as many others which have been allowed to pass without a remark. He says (p. 146). "Whether the presence of specific sensitizing antibodies affords an effective resistance against the corresponding bacterium we do not know. We should clearly expect that an individual possessing an antibody acting on the surface antigen of a particular bacterial parasite would be more resistant to this organism than another individual from whose blood this antibody was absent." We think that the evidence afforded by the work of *Solis-Cohen*, *Robertson* and *Sia*, *Bull* and *McKee* specially with the counter-proof of the absorption test, cannot on the whole be called "scanty."

Proceeding further when the author makes a brief mention of the transmissible lytic agents, we slightly disagree with his method of tackling the subject. Too much emphasis is given to the actual tests of the therapeutic action *in vivo*, when he concludes that the prospects of an inquiry in that direction seem hardly hopeful. The subject of

the Bacteriophage has suffered from the very beginning, from a sort of recklessness, speculation and impatience for results, which were the peculiar characteristics of its worthy champion D'HERELLE. The prospects of the enquiry, I am persuaded, would be more hopeful if attention was paid to the pure knowledge of its nature. Then—and the colloidal theories mentioned by the author (p. 376) will support my contention—we could gain a better control over its behaviour.

The author can hardly be blamed if the chapter on a subject in a formative stage and with such a cumbrous literature and so much experimental evidence as anaphylaxis, hyper-sensitiveness and allergy gives the impression of a less digested treatment. It is, all the same, a clear source of information.

Used as we are, while reading the book, to the apt comments and the appropriate analysis of many real problems, we are sometimes somewhat disappointed in not finding the author clearly expressing himself on certain matters which we, personally, would have liked to find more fully discussed. For example, the negative phase in the response to antigen injection (pp 171-177).

It may appear that, through fear or through anxiety to be fair, in several cases, no attempt at co-ordination has been made. And yet the fact often observed in our sciences is that without abandoning our theories, we can still defend our particular tenets by carefully combining the established facts with probable occurrences. Leaving out EIRLICH, the past master not only in illuminating the way to many difficult problems, but also in cleverly and almost humorously conjuring up a host of convenient fluid or solid entities with determined function to perform, we find ourselves in our more scared age, resorting also to clever dodgings and laborious straining of our scientific conquests in order to explain several phenomena which come to mar our short-lived enthusiasm for a newly formed theory. Talking of only a minor point, one instance among many which may be cited is the manner in which we explain away the age fluctuation observed in skin-sensibility towards diphtheria toxin.

In the present condition and outlook of this science, which has to deal with subtle and complex phenomena of what we may call overactivated physiology and impalpable biochemistry, it is not unscientific to offer facts arranged in the light of a theory, provided that the objections which arise from further investigation are not distorted to suit any convenient solution. An independent thinker, Mr. Topley to my judgment, is fair in his treatment and sharp in his analysis of all but perhaps some very minor points.

The author is very modest in his claim that the book is a mere Outline intended mainly for medical students. It is more than that and even specialists, besides the real pleasure which they will experience in reading the book, will find much food for thought.

G. PALACIOS

*Human Embryology and Morphology* By SIR ARTHUR KEITH  
M D., F.R.S. Fifth edition. (Edward Arnold & Co.) London.  
1933, 32s. 6d

The latest edition of Sir Arthur Keith's *Human Embryology and Morphology* has an individuality all its own. The author who is our one of the foremost authorities on evolution has discussed the embryology and comparative anatomy as revealers of the mechanism of Evolution.

Every stage has been traced in the embryo which marks a new adaptive phase to the varying environment that confronts it and as far as possible the corresponding parallel from phylogeny is simultaneously depicted. This method of studying the ontogeny and phylogeny has enormous advantages in the advancement of further research into many obscure problems in physiology and pathology and to that extent this book serves as a valuable guide to workers in these branches of medical science. The Experimental Embryology with the aid of the advancing methods of Tissue Culture technique is another hopeful avenue through which the inter-relation between the various organs of the embryo can be studied as regards their position, growth and functions. The Chemical Embryology and, particularly, the work of Prof. C M Child on metabolic gradients which have not been given enough space in this book are the methods which may ultimately yield results not to be despised by the student of evolution.

Finally, the mechanism of the chromosomes and of the genes that are responsible for the transmission of various traits of the parents into their offspring require a good deal of attention than that received at the hands of the author, if the medical student for whom the present book is intended, is to realise the prospects offered by this branch of science in clearing up many problems of normal and abnormal heredity. The marvellous work of T H. Morgan on the genes of the *Drosophila* must serve as a stimulus for similar work on higher animals on account of the tissue culture methods.

As one goes through the work one gets the impression that the evidence afforded by comparative anatomy is rather unequally distributed among the various systems. The circulatory, digestive and visual

systems especially do not get their adequate share. On the other hand, the skeletal and the locomotor systems, the face, the pharynx and the teeth have been very fully and excellently dealt with. On the whole, one can detect more or less a distinct, though unconscious, surgical bias in the stress put on the aspects, normal and abnormal, of embryology. The author seems to be too much apprehensive about the bulk of the book getting out of control, but one does not agree on this point with the author, for in the incomplete state of our knowledge in this branch, its treatment from different points of view, which is the speciality of this book, cannot be too sufficiently dealt with.

The value of this book is enhanced by useful notes appended at the end of every chapter and the liberal use made of illustrations which enable the student to grasp the phases of development more easily and accurately than from mere descriptions.

One specially realises the usefulness of this book for the medical colleges in India, particularly in this presidency, where comparative anatomy or zoology is not studied or taught in the department of anatomy. The book will prove an asset to the students who for want of actual firsthand knowledge are confused when confronted with the study of embryology

D. B. S.

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*Shiraki (Tokuichi)*—A systematic study of Tryptidae in the Japanese Empire—(Memoirs of the Faculties of Science & Agriculture, Taihoku Imperial University, Vol VIII, July, 1933)—Formosa (Japan), 1933

*Maniferos Fossiles de la Republica Argentina por Florentino Ameghino*—Vol. IX (Atlas)—La Plata, 1932.

*The University of Lucknow* Abstracts of Publications by members of the University, 1928-1932 (Faculty of Medicine) Lucknow, 1933.

*An Outline of Immunity* by W. W. C. Topley, (Edward Arnold & Co.) London, 1933, 18s. net.

*Practical Anatomy by six teachers.* Ed. by E. P. Stibbe, F. R. C. S. (Ed. Arnold & Co.) London, 1932. 30s. net.

*Human Embryology and Morphology* by Sir Arthur Keith, Fifth edition. (Arnold). London, 1933. 32s. 6d. net.

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## Acknowledgments

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